Isothermal Vapor−Liquid Equilibria for Benzene + Cyclohexane + 1-Propanol and for Three Constituent Binary Systems

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Isothermal vapor−liquid equilibria were measured for the ternary system of benzene + cyclohexane + 1-propanol and its constituent binary systems of benzene + cyclohexane, cyclohexane + 1-propanol, and benzene + 1-propanol at 323.15 and 333.15 K, using the apparatus proposed in a previous study. The experimental binary data were correlated using the NRTL equation. The ternary system was predicted using the binary NRTL parameters. The average absolute percent deviations between the predicted and experimental ternary total pressures are 0.5% at 323.15 K and 0.4% at 333.15 K.

Introduction

The availability of azeotropic data for multicomponent systems is important for the design and operation of separation processes. This paper discusses the vapor−liquid equilibria (VLE) and azeotropic data that were measured for the ternary system of benzene + cyclohexane + 1-propanol and its constituent binary systems of benzene + cyclohexane, cyclohexane + 1-propanol, and benzene + 1-propanol at 323.15 and 333.15 K. All these ternary and binary systems form a maximum pressure azeotrope, and each azeotropic point was determined on the basis of the experimental VLE data. For the ternary system, three data sets of isobaric VLE at 101.3 kPa are available in the literature (Morachevsky and Ch'eng, 1961; Arce et al., 1986; Hiaki et al., 1986).

Experimental Section

Apparatus and Procedure. In this VLE measurement, a modified Rogalski-Malanowski equilibrium still combined with an isothermal VLE measuring apparatus (Kurihara et al., 1995) was used. The apparatus contained an ebulliometer for the reference substance (water) in addition to this equilibrium still for samples.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of ±0.01 K. The pressure in the still was determined by measuring the bubble point of water and referring to the vapor pressure data of water (Bridgeman and Aldrich, 1964). The accuracy was estimated to be ±0.03 kPa.

Analysis. Vapor and liquid samples were analyzed with a Shimadzu gas chromatograph type GC-8AIT equipped with a thermal conductivity cell. Chromosorb W was used as the column packing, and helium, as the carrier gas. The compositions were determined by the relative area method with an accuracy of ±0.001 mole fraction.

Materials. Benzene, cyclohexane, and 1-propanol were special grade pure reagents (Wako Pure Chemical Industry, Ltd.) and were used after removing any traces of water with molecular sieves. The purity of the materials was checked by gas chromatography and found to be better than 99.9 mol %. In Table 1, some measured properties of the purified reagents are shown along with the literature values.

Experimental Results

Binary Systems. The VLE data at 323.15 and 333.15 K for the three binary systems are shown in Tables 2−4 and Figures 1 and 2. The activity coefficients, γ_i, in the tables and figures were evaluated by the following equation:

$$\varphi_i P y_i = x_i \gamma_i P_i^S \varphi_i^S \exp[\nu_i^L (P - P_i^S)/RT] \quad (1)$$

where φ_i and φ_i^S are the fugacity coefficients of component i in the mixture and the pure vapor, respectively. They were calculated using the second virial coefficients obtained

Table 1. Densities, ρ, and Normal Boiling Points, T_b, of the Components

	ρ(298.15 K)/g cm^{-3}		T_b/K	
component	exptl	lit.[a]	exptl	lit.[a]
benzene	0.8736	0.873 60	353.20	353.244
cyclohexane	0.7739	0.773 89	353.83	353.880
1-propanol	0.7996	0.799 60	370.17	370.301

[a] Riddick et al., 1986.

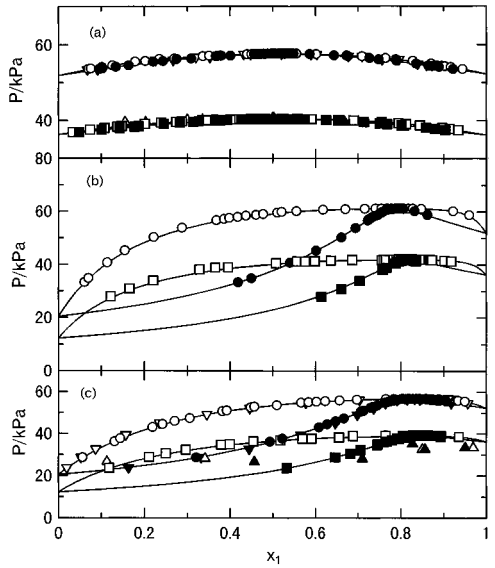

Figure 1. Pressure−composition diagram for the binary systems. (a) Benzene (1) + cyclohexane (2): (△, ▲) literature (Morachevsky and Zharov, 1963) x_1 and y_1 at 323.15 K; (▽, ▼) literature (Boublik, 1963) x_1 and y_1 at 333.15 K. (b) Cyclohexane (1) + 1-propanol (2). (c) Benzene (1) + 1-propanol (2): (△, ▲) literature (Arce et al., 1977) x_1 and y_1 at 323.15 K (▽, ▼) literature (Udovenko and Mazanko, 1972) x_1 and y_1 at 333.15 K. (a), (b), (c): (□, ■) experimental x_1 and y_1 at 323.15 K; (○, ●) experimental x_1 and y_1 at 333.15 K; (−) NRTL equation.

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Table 2. Isothermal Vapor−Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for Benzene (1) + Cyclohexane (2)

P/kPa	x_1	y_1	γ_1	γ_2
		323.15 K		
36.88	0.034	0.048	1.440	1.002
37.48	0.074	0.101	1.414	1.003
37.94	0.107	0.142	1.391	1.005
38.31	0.138	0.177	1.357	1.008
38.42	0.147	0.187	1.350	1.009
39.05	0.201	0.245	1.314	1.016
39.36	0.239	0.282	1.282	1.023
39.57	0.274	0.314	1.251	1.030
39.67	0.287	0.326	1.243	1.033
39.99	0.335	0.366	1.205	1.050
40.03	0.347	0.378	1.203	1.050
39.96	0.348	0.378	1.197	1.050
40.09	0.365	0.393	1.191	1.055
40.21	0.404	0.426	1.169	1.066
40.27	0.422	0.441	1.161	1.072
40.27	0.434	0.452	1.157	1.074
40.31	0.448	0.463	1.149	1.080
40.40	0.463	0.474	1.140	1.090
40.32	0.477	0.486	1.133	1.091
40.33	0.493	0.497	1.121	1.102
40.33	0.497	0.500	1.119	1.104
40.35	0.509	0.510	1.115	1.109
40.35	0.524	0.522	1.108	1.116
40.33	0.531	0.527	1.104	1.120
40.31	0.560	0.550	1.092	1.135
40.27	0.591	0.574	1.078	1.155
40.07	0.657	0.626	1.053	1.204
39.95	0.690	0.653	1.042	1.232
39.55	0.755	0.714	1.031	1.273
39.22	0.795	0.751	1.022	1.313
39.02	0.812	0.768	1.018	1.328
38.68	0.844	0.801	1.013	1.361
38.05	0.897	0.858	1.004	1.448
37.81	0.914	0.879	1.003	1.469
37.47	0.934	0.904	1.001	1.505
		333.15 K		
53.56	0.070	0.095	1.393	1.003
53.68	0.076	0.102	1.380	1.004
54.10	0.102	0.134	1.361	1.004
54.48	0.126	0.164	1.358	1.003
55.48	0.178	0.221	1.318	1.011
55.61	0.202	0.243	1.280	1.015
56.19	0.234	0.275	1.263	1.023
56.28	0.270	0.309	1.231	1.024
56.93	0.336	0.367	1.188	1.043
57.02	0.351	0.380	1.180	1.047
57.03	0.374	0.401	1.168	1.049
57.44	0.440	0.456	1.137	1.073
57.46	0.450	0.465	1.134	1.074
57.49	0.461	0.473	1.127	1.081
57.52	0.471	0.481	1.122	1.085
57.56	0.478	0.487	1.120	1.087
57.59	0.488	0.495	1.116	1.092
57.60	0.499	0.503	1.109	1.098
57.61	0.509	0.511	1.104	1.103
57.62	0.518	0.519	1.102	1.105
57.62	0.528	0.527	1.098	1.110
57.61	0.533	0.531	1.096	1.112
57.60	0.538	0.535	1.094	1.115
57.59	0.547	0.542	1.090	1.119
57.57	0.556	0.549	1.085	1.124
57.43	0.602	0.587	1.069	1.146
57.13	0.673	0.644	1.044	1.196
56.89	0.709	0.677	1.037	1.215
56.42	0.764	0.727	1.025	1.256
56.13	0.788	0.749	1.019	1.279
55.69	0.828	0.790	1.015	1.310
54.96	0.870	0.836	1.009	1.336
54.43	0.895	0.865	1.005	1.349
54.30	0.903	0.873	1.003	1.371
54.10	0.917	0.889	1.003	1.395
53.58	0.944	0.922	1.001	1.440

Table 3. Isothermal Vapor−Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for Cyclohexane (1) + 1-Propanol (2)

P/kPa	x_1	y_1	γ_1	γ_2
		323.15 K		
27.92	0.122	0.614	3.907	1.001
30.85	0.166	0.661	3.408	1.022
33.92	0.221	0.704	2.991	1.050
38.08	0.329	0.757	2.418	1.124
38.81	0.366	0.766	2.241	1.167
38.90	0.396	0.766	2.076	1.228
40.51	0.508	0.788	1.731	1.423
41.15	0.557	0.794	1.616	1.560
41.14	0.576	0.793	1.560	1.637
41.28	0.599	0.795	1.509	1.720
41.51	0.636	0.801	1.439	1.850
41.75	0.687	0.808	1.352	2.088
41.78	0.755	0.815	1.241	2.573
41.83	0.760	0.818	1.239	2.587
41.87	0.765	0.816	1.229	2.674
41.96	0.783	0.819	1.208	2.855
41.99	0.790	0.821	1.201	2.920
42.02	0.795	0.818	1.190	3.043
42.07	0.810	0.821	1.173	3.233
42.06	0.829	0.824	1.150	3.532
41.99	0.847	0.827	1.128	3.874
41.87	0.865	0.832	1.108	4.253
41.82	0.870	0.831	1.099	4.437
41.77	0.873	0.834	1.098	4.457
41.55	0.902	0.830	1.052	5.883
41.38	0.918	0.835	1.036	6.798
		333.15 K		
33.33	0.061	0.419	4.482	1.008
34.85	0.070	0.450	4.381	1.007
40.68	0.114	0.541	3.759	1.029
45.25	0.155	0.602	3.411	1.039
50.21	0.222	0.661	2.892	1.067
53.79	0.288	0.694	2.502	1.127
56.65	0.368	0.723	2.144	1.210
57.11	0.386	0.725	2.066	1.246
57.52	0.398	0.730	2.031	1.257
57.88	0.418	0.733	1.954	1.294
58.36	0.437	0.739	1.899	1.318
58.65	0.461	0.745	1.823	1.352
58.95	0.478	0.748	1.774	1.387
59.53	0.511	0.754	1.689	1.460
59.80	0.521	0.755	1.666	1.491
60.06	0.556	0.760	1.578	1.583
60.70	0.618	0.769	1.451	1.790
60.85	0.670	0.780	1.361	1.979
61.08	0.716	0.785	1.286	2.256
61.10	0.741	0.786	1.245	2.463
61.13	0.755	0.789	1.227	2.569
61.16	0.768	0.791	1.209	2.689
61.16	0.778	0.791	1.194	2.810
61.17	0.787	0.792	1.182	2.915
61.17	0.807	0.798	1.161	3.126
61.16	0.817	0.799	1.148	3.280
61.14	0.828	0.801	1.136	3.454
61.09	0.848	0.806	1.115	3.808
60.21	0.922	0.832	1.043	6.345
58.74	0.960	0.862	1.013	9.935

by the Tsonopoulos method (Tsonopoulos, 1974). The binary constants in the Tsonopoulos method were set as 0.017 for the benzene + cyclohexane system and 0.150 for the cyclohexane + 1-propanol and benzene + 1-propanol systems. The value for the systems containing 1-propanol are those recommended by Tsonopoulos. For the benzene + cyclohexane system, the binary constant is determined from the second virial coefficients reported by Waelbroeck (1955). The liquid molar volumes, v_i^L, were calculated by the modified Rackett equation (Spencer and Adler, 1978). The vapor pressures of the pure components, P_i^S, were calculated from the Antoine equation constants given in Table 5. The Antoine constants were determined from the

Table 4. Isothermal Vapor−Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fractions, and Activity Coefficients, γ_i, for Benzene (1) + 1-Propanol (2)

P/kPa	x_1	y_1	γ_1	γ_2
		323.15 K		
22.02	0.101	0.493	3.002	1.014
23.58	0.119	0.533	2.946	1.021
28.76	0.211	0.647	2.451	1.050
30.54	0.250	0.682	2.312	1.056
32.23	0.297	0.706	2.124	1.099
34.60	0.380	0.744	1.875	1.165
34.90	0.399	0.746	1.806	1.203
36.23	0.455	0.767	1.689	1.263
36.90	0.518	0.779	1.534	1.380
37.64	0.570	0.791	1.443	1.492
37.60	0.592	0.796	1.397	1.534
38.23	0.655	0.808	1.302	1.736
38.94	0.688	0.816	1.275	1.874
39.06	0.764	0.832	1.174	2.271
39.06	0.805	0.843	1.129	2.569
39.15	0.817	0.844	1.116	2.727
39.19	0.828	0.845	1.104	2.886
39.10	0.832	0.849	1.101	2.872
39.25	0.843	0.851	1.093	3.044
39.27	0.849	0.853	1.089	3.125
39.24	0.856	0.856	1.083	3.208
39.25	0.867	0.860	1.074	3.378
39.22	0.877	0.864	1.066	3.546
39.18	0.885	0.868	1.060	3.678
39.14	0.893	0.871	1.053	3.860
38.64	0.936	0.893	1.017	5.291
		333.15 K		
28.61	0.057	0.321	3.138	1.009
36.16	0.131	0.493	2.636	1.031
37.59	0.144	0.523	2.641	1.024
43.03	0.219	0.609	2.307	1.052
44.43	0.242	0.627	2.217	1.067
45.92	0.270	0.648	2.121	1.081
47.23	0.306	0.666	1.977	1.109
50.56	0.382	0.706	1.793	1.174
50.91	0.392	0.713	1.776	1.173
52.41	0.448	0.730	1.637	1.251
52.75	0.457	0.734	1.624	1.261
53.53	0.510	0.746	1.500	1.354
54.71	0.567	0.761	1.405	1.474
54.96	0.584	0.766	1.380	1.509
55.19	0.603	0.770	1.348	1.561
55.46	0.623	0.775	1.320	1.616
55.83	0.656	0.782	1.273	1.728
56.22	0.697	0.793	1.223	1.877
56.55	0.765	0.809	1.143	2.247
56.61	0.783	0.814	1.125	2.373
56.68	0.803	0.820	1.106	2.533
56.70	0.821	0.828	1.093	2.666
56.70	0.843	0.837	1.076	2.882
56.67	0.858	0.843	1.064	3.068
56.62	0.874	0.849	1.051	3.324
56.52	0.889	0.857	1.041	3.568
56.37	0.904	0.866	1.032	3.858
56.28	0.909	0.870	1.029	3.943
56.24	0.913	0.873	1.027	4.027
56.13	0.919	0.878	1.025	4.148
55.96	0.928	0.885	1.020	4.387
55.91	0.932	0.889	1.019	4.481
55.84	0.934	0.890	1.017	4.569
55.43	0.950	0.906	1.010	5.121

vapor pressure data of the pure components measured in this work. The average absolute percent deviations between the values calculated by the Antoine equation and the experimental values are less than about 0.1% in all cases.

The experimental VLE data were examined using the thermodynamic consistency test (Kojima et al., 1990) which was proposed in our previous paper. The results indicate that the reported data for the three systems are thermodynamically consistent.

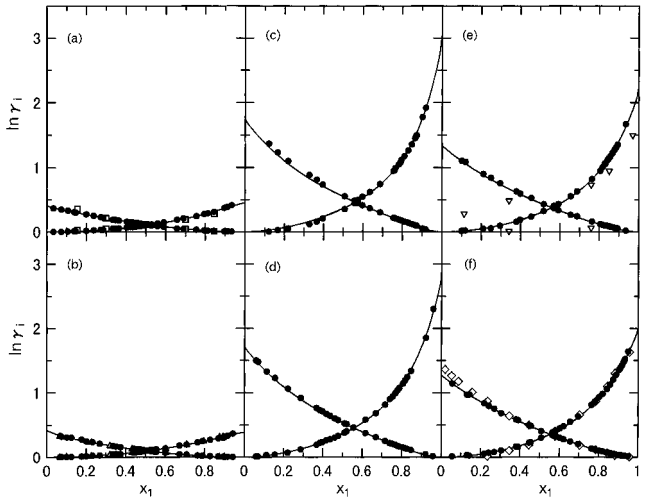

Figure 2. Activity coefficient−liquid composition diagram for the binary systems (a) benzene (1) + cyclohexane (2) at 323.15 K, (b) benzene (1) + cyclohexane (2) at 333.15 K, (c) cyclohexane (1) + 1-propanol (2) at 323.15 K, (d) cyclohexane (1) + 1-propanol (2) at 333.15 K, (e) benzene (1) + 1-propanol (2) at 323.15 K, and (f) benzene (1) + 1-propanol (2) at 333.15 K: (●) experimental; (□) Morachevsky and Zharov (1963); (△) Boublik (1963); (▽) Arce et al. (1977); (◇) Udovenko and Mazanko (1972); (—) NRTL equation.

Table 5. Antoine Constants of Components[a]

component	A	B	C
benzene	6.082 00	1237.868	−49.479
cyclohexane	6.172 14	1318.971	−37.218
1-propanol	6.958 81	1492.106	−69.091

[a] $\log(P/\text{kPa}) = A - B/[(T/\text{K}) + C]$.

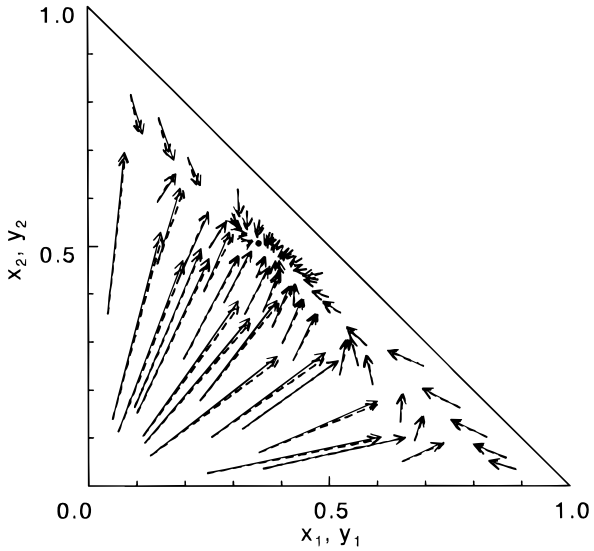

Figure 3. Vapor−liquid equilibrium tie lines (tails of arrows represent liquid-phase mole fractions x_1 and x_2, and heads of arrows represent vapor-phase mole fractions y_1 and y_2) for benzene (1) + cyclohexane (2) + 1-propanol (3) at 323.15 K: (—) this work; (- - -) NRTL equation; (●) azeotropic point.

For the benzene + cyclohexane and benzene + 1-propanol systems at the temperatures investigated in this paper, there are four data sets, which contain pressure, liquid composition, and vapor composition, available in the literature. However, these data are not consistent with our proposed test except for the data reported by Boublik (1963) for the benzene + cyclohexane system. VLE data for the cyclohexane + 1-propanol system at 323.15 and 333.15 K are not available in the literature. Figures 1 and 2 shows the comparisons of all literature VLE data and our results.

Table 6. Isothermal Vapor−Liquid Equilibrium Data, Vapor Pressure, P, Liquid Phase, x_i, and Vapor Phase, y_i, Mole Fractions, and Activity Coefficients, γ_i, for Benzene (1) + Cyclohexane (2) + 1-Propanol (3)

P/kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	P/kPa	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
323.15 K															
39.47	0.040	0.358	0.076	0.695	2.073	2.113	1.223	36.12	0.363	0.036	0.657	0.100	1.808	2.776	1.191
31.86	0.050	0.139	0.151	0.529	2.671	3.362	1.025	43.38	0.363	0.363	0.394	0.443	1.297	1.456	2.104
30.80	0.062	0.114	0.197	0.469	2.718	3.516	1.018	43.76	0.377	0.527	0.366	0.503	1.170	1.148	4.876
42.52	0.089	0.815	0.113	0.734	1.489	1.053	5.532	43.79	0.382	0.524	0.371	0.501	1.171	1.151	4.870
35.45	0.096	0.165	0.234	0.495	2.393	2.941	1.059	43.20	0.382	0.331	0.418	0.416	1.302	1.494	2.037
34.92	0.101	0.153	0.251	0.474	2.404	2.993	1.049	44.00	0.389	0.452	0.388	0.469	1.209	1.255	3.229
32.67	0.113	0.104	0.311	0.385	2.494	3.352	1.034	43.74	0.397	0.512	0.379	0.492	1.150	1.156	5.064
31.84	0.117	0.089	0.334	0.349	2.522	3.463	1.036	43.91	0.399	0.439	0.397	0.460	1.203	1.265	3.163
30.17	0.129	0.063	0.392	0.270	2.546	3.590	1.029	42.99	0.403	0.297	0.443	0.389	1.302	1.550	1.963
42.44	0.143	0.463	0.191	0.620	1.564	1.564	1.659	43.70	0.416	0.494	0.395	0.477	1.143	1.160	5.076
43.17	0.145	0.592	0.183	0.649	1.502	1.302	2.249	43.74	0.424	0.491	0.402	0.473	1.142	1.158	5.254
42.98	0.147	0.766	0.178	0.679	1.435	1.048	5.769	42.70	0.425	0.263	0.472	0.358	1.307	1.600	1.897
42.77	0.190	0.436	0.249	0.567	1.546	1.530	1.715	43.80	0.426	0.377	0.428	0.420	1.212	1.342	2.757
40.90	0.198	0.266	0.312	0.480	1.779	2.034	1.293	43.68	0.443	0.473	0.418	0.461	1.135	1.170	5.140
43.56	0.208	0.683	0.232	0.625	1.339	1.096	4.665	43.73	0.452	0.452	0.427	0.449	1.138	1.194	4.614
39.34	0.232	0.178	0.391	0.386	1.831	2.354	1.211	43.71	0.473	0.423	0.445	0.429	1.132	1.219	4.325
43.00	0.240	0.406	0.293	0.529	1.447	1.541	1.762	43.52	0.486	0.444	0.445	0.438	1.097	1.181	5.944
32.39	0.247	0.027	0.608	0.102	2.210	3.393	1.055	43.63	0.498	0.393	0.465	0.405	1.122	1.236	4.249
43.73	0.251	0.497	0.286	0.550	1.373	1.331	2.320	42.70	0.522	0.233	0.535	0.305	1.206	1.539	2.275
37.40	0.256	0.102	0.492	0.277	1.987	2.806	1.097	43.54	0.523	0.361	0.487	0.384	1.116	1.274	3.954
43.10	0.282	0.382	0.337	0.488	1.420	1.515	1.830	42.93	0.560	0.252	0.543	0.308	1.147	1.444	2.776
43.92	0.296	0.557	0.306	0.547	1.251	1.186	3.584	43.22	0.577	0.293	0.536	0.331	1.106	1.343	3.611
44.00	0.309	0.539	0.318	0.536	1.247	1.203	3.448	42.56	0.590	0.212	0.577	0.273	1.147	1.509	2.631
43.52	0.310	0.617	0.312	0.562	1.207	1.090	6.136	41.54	0.648	0.134	0.651	0.191	1.150	1.632	2.457
44.02	0.319	0.525	0.329	0.526	1.250	1.212	3.339	39.84	0.653	0.050	0.733	0.089	1.234	1.957	1.948
39.34	0.320	0.119	0.517	0.269	1.755	2.454	1.223	40.89	0.677	0.095	0.693	0.145	1.154	1.721	2.371
43.18	0.325	0.358	0.373	0.454	1.366	1.507	1.921	42.07	0.696	0.250	0.622	0.283	1.036	1.311	6.057
43.81	0.329	0.572	0.330	0.539	1.210	1.135	4.734	41.31	0.771	0.163	0.694	0.203	1.025	1.417	5.275
44.02	0.333	0.508	0.340	0.513	1.238	1.222	3.320	40.51	0.827	0.100	0.753	0.138	1.017	1.541	4.950
43.84	0.349	0.435	0.365	0.478	1.263	1.325	2.599	39.88	0.867	0.059	0.799	0.086	1.013	1.603	5.071
37.81	0.354	0.069	0.600	0.176	1.771	2.665	1.197	39.43	0.888	0.034	0.832	0.052	1.019	1.664	4.799
43.81	0.355	0.553	0.349	0.527	1.186	1.148	4.824								
333.15 K															
57.98	0.188	0.223	0.306	0.441	1.805	2.208	1.214	63.30	0.314	0.522	0.314	0.518	1.207	1.205	3.167
58.15	0.322	0.151	0.468	0.293	1.616	2.173	1.286	62.76	0.261	0.437	0.292	0.509	1.340	1.403	2.017
55.65	0.244	0.136	0.421	0.312	1.838	2.462	1.168	63.46	0.193	0.586	0.212	0.600	1.330	1.246	2.634
59.94	0.705	0.117	0.677	0.159	1.098	1.567	2.700	61.17	0.276	0.285	0.353	0.427	1.494	1.761	1.494
59.57	0.654	0.106	0.664	0.153	1.154	1.655	2.219	58.91	0.746	0.074	0.722	0.111	1.088	1.701	2.673
57.68	0.502	0.076	0.637	0.142	1.399	2.077	1.474	62.63	0.560	0.344	0.506	0.360	1.078	1.258	4.278
56.87	0.051	0.314	0.094	0.633	2.008	2.208	1.191	62.98	0.515	0.316	0.489	0.353	1.140	1.350	2.877
60.94	0.106	0.839	0.119	0.752	1.306	1.048	7.004	62.65	0.478	0.288	0.474	0.344	1.185	1.437	2.378
62.09	0.097	0.769	0.110	0.715	1.344	1.108	3.962	61.92	0.458	0.498	0.425	0.466	1.095	1.112	7.518
62.16	0.089	0.705	0.104	0.702	1.387	1.188	2.857	63.41	0.415	0.449	0.395	0.451	1.150	1.222	3.509
61.76	0.075	0.604	0.096	0.692	1.510	1.358	1.989	63.31	0.365	0.394	0.378	0.446	1.250	1.375	2.257
30.78	0.033	0.031	0.168	0.205	3.047	3.993	1.009	39.53	0.010	0.100	0.036	0.495	2.753	3.813	1.017
61.44	0.191	0.365	0.253	0.521	1.554	1.685	1.524	60.57	0.384	0.593	0.381	0.547	1.146	1.072	9.317
61.73	0.658	0.236	0.598	0.268	1.069	1.346	3.819	63.16	0.355	0.549	0.343	0.515	1.163	1.136	4.569
58.71	0.434	0.118	0.575	0.208	1.486	1.992	1.387	63.48	0.316	0.489	0.322	0.504	1.233	1.255	2.765
49.94	0.306	0.020	0.628	0.062	1.968	2.998	1.120	63.20	0.291	0.452	0.313	0.500	1.296	1.341	2.244
57.19	0.848	0.017	0.823	0.025	1.060	1.621	3.153	49.98	0.155	0.099	0.386	0.347	2.389	3.388	0.874
57.17	0.796	0.015	0.802	0.024	1.100	1.763	2.575	62.51	0.236	0.688	0.242	0.617	1.223	1.075	5.674
63.03	0.471	0.452	0.436	0.439	1.112	1.174	5.009	63.23	0.213	0.625	0.226	0.601	1.280	1.166	3.297
63.42	0.395	0.378	0.400	0.424	1.224	1.365	2.400	63.54	0.294	0.579	0.296	0.548	1.220	1.153	3.814
63.56	0.229	0.520	0.251	0.559	1.329	1.310	2.347	63.65	0.271	0.534	0.285	0.543	1.276	1.241	2.741
55.07	0.547	0.014	0.733	0.031	1.412	2.354	1.445	62.29	0.172	0.745	0.186	0.655	1.285	1.051	5.834
53.68	0.961	0.031	0.936	0.044	1.000	1.470	6.623	62.90	0.153	0.666	0.170	0.647	1.334	1.172	3.105
57.01	0.881	0.028	0.830	0.041	1.026	1.608	3.963	62.31	0.125	0.546	0.156	0.634	1.485	1.389	1.939
59.05	0.783	0.180	0.719	0.209	1.034	1.318	5.647	51.10	0.074	0.153	0.188	0.490	2.494	3.165	1.038

Ternary System. Table 6 and Figures 3 and 4 give the experimental VLE data for the ternary system of benzene + cyclohexane + 1-propanol at 323.15 and 333.15 K. The tails of the solid arrows in Figures 3 and 4 represent experimental liquid compositions, and the heads of the arrows show experimental vapor compositions on the same tie line.

Azeotropic Data. The binary maximum pressure azeotropic points at each temperature were determined from the experimental VLE data using a graphical technique (Hiaki et al., 1986). The determination of the ternary maximum pressure azeotropic point was also performed by means of modifying the program of Hiaki et al. (1986) for isobaric data. The evaluated binary and ternary azeotropic compositions and pressures are shown in Table 7 and are compared with some literature values in Figures 5 and 6.

Table 7. Azeotropic Composition $x_{i(az)}$ in Mole Fraction and Pressure $P_{(az)}$ for the Three Binary Systems and the Ternary System

T/K	$x_{1(az)}$	$x_{2(az)}$	$P_{(az)}$/kPa
Benzene (1) + Cyclohexane (2)			
323.15	0.513	0.487	40.36
333.15	0.522	0.478	57.62
Cyclohexane (1) + 1-Propanol (2)			
323.15	0.822	0.178	42.06
333.15	0.794	0.206	61.18
Benzene (1) + 1-Propanol (2)			
323.15	0.855	0.145	39.27
333.15	0.832	0.168	56.70
Benzene (1) + Cyclohexane (2) + 1-Propanol (3)			
323.15	0.354	0.505	44.03
333.15	0.325	0.508	63.77

Table 8. Parameters and Deviations between the Calculated and Experimental Vapor-Phase Mole Fractions, Δy_i, and Pressures, ΔP, for the NRTL Equation[a]

NRTL param	benzene (1) + cyclohexane (2)	cyclohexane (1) + 1-propanol (2)	benzene (1) + 1-propanol (2)	benzene (1) + cyclohexane (2) + 1-propanol (3)
		323.15 K		
$g_{12} - g_{22}$[b]	166.1437	757.1052	552.4479	no ternary
$g_{21} - g_{11}$[b]	−14.1638	340.8796	230.9265	parameters
α_{12}	0.3	0.53	0.59	
		333.15 K		
$g_{12} - g_{22}$[b]	97.8224	724.0679	513.2185	no ternary
$g_{21} - g_{11}$[b]	37.6067	339.5263	217.1249	parameters
α_{12}	0.3	0.53	0.59	

T/K	ΔP/%	$100\Delta y_1$	ΔP/%	$100\Delta y_1$	ΔP/%	$100\Delta y_1$	ΔP/%	$100\Delta y_1$	$100\Delta y_2$
323.15	0.1	0.1	0.8	0.6	0.7	0.3	0.4	0.3	0.4
333.15	0.1	0.1	0.5	0.4	0.2	0.2	0.4	0.3	0.4

[a] $\Delta y_i = \sum_k |y_{i,\text{exptl}} - y_{i,\text{calcd}}|_k/N$, $\Delta P = 100 \sum_k (|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|_k/N$. [b] K, N = number of data points.

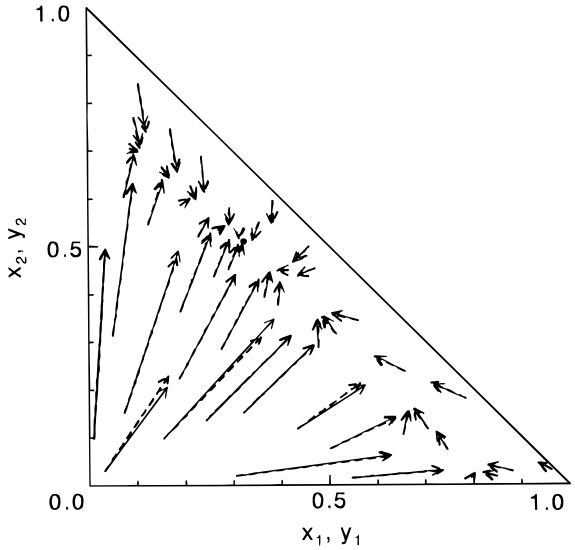

Figure 4. Vapor-liquid equilibrium tie lines (tails of arrows represent liquid-phase mole fractions x_1 and x_2, and heads of arrows represent vapor-phase mole fractions y_1 and y_2) for benzene (1) + cyclohexane (2) + 1-propanol (3) at 333.15 K: (—) this work; (- - -) NRTL equation; (●) azeotropic point.

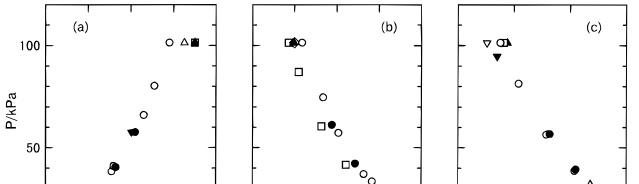

Figure 5. Azeotropic pressure−liquid composition diagram for the binary systems. (a) Benzene (1) + cyclohexane (2): (○) Storonkin and Morachevsky (1957); (□) Morachevsky and Zharov (1963); (▼) Boublik (1963); (▲) Darmois and Darmois (1964); (△) Donald and Ridgway (1958). (b) Cyclohexane (1) + 1-propanol (2): (○) Storonkin and Morachevsky (1957); (□) Brzostowski and Warycha (1963); (▲) Svoboda et al. (1977); (◇) Morachevsky and Ch'eng (1961). (c) Benzene (1) + 1-propanol (2): (○) Storonkin and Morachevsky (1957); (▼) Fu and Lu (1966); (▲) Tojo et al. (1973); (△) Brown and Smith (1959); (▽) Morachevsky and Ch'eng (1961); (□) Young and Fortey (1902). (a), (b), (c): (●) this work.

Correlation and Prediction

The activity coefficients of the binary systems were correlated using the NRTL equation (Renon and Prausnitz, 1968) at each of the equilibrium temperatures. Table 8 lists the NRTL parameters $g_{12} - g_{22}$, $g_{21} - g_{11}$, and α_{12} of the binary systems and the results. In the table, ΔP is the average absolute percent deviation in total pressure and Δy_i is the average absolute deviation in vapor phase mole fraction of component i. In Figures 1 and 2, the correlated results are shown by the solid lines.

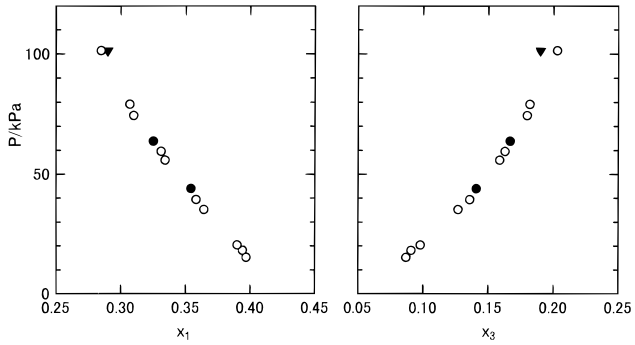

Figure 6. Azeotropic pressure−liquid composition diagram for benzene (1) + cyclohexane (2) + 1-propanol (3): (●) this work; (○) Storonkin et al. (1957); (▼) Arce et al. (1986).

The VLE of the ternary system of benzene + cyclohexane + 1-propanol was predicted using the binary NRTL parameters in Table 8. The results are summarized in Table 8 and also illustrated by the broken arrows in Figures 3 and 4. The NRTL equation provides good predictions for the ternary system at both temperatures.

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