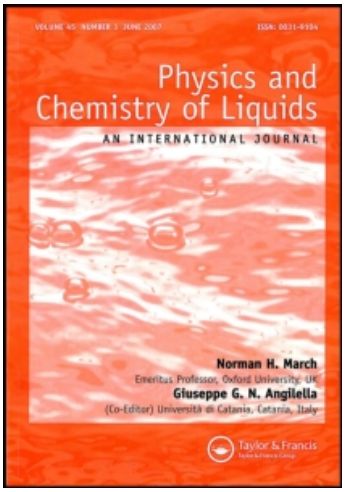

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Vapor-Liquid Equilibria in the Ternary System 2-Chlorobutane 1-Chlorobutane Cyclohexane and Its Binaries

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VAPOR-LIQUID EQUILIBRIA IN THE TERNARY SYSTEM 2-CHLOROBUTANE + 1-CHLOROBUTANE + CYCLOHEXANE AND ITS BINARIES

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Vapor-liquid equilibrium at 101.3 kPa has been determined for the ternary system 2-chlorobutane + 1-chlorobutane + cyclohexane and its binaries 2-chlorobutane + cyclohexane and 1-chlorobutane + cyclohexane. The binary system 1-chlorobutane + cyclohexane presents an azeotropic point at 76.86 C that contains 57.5% mol 1-chlorobutane. No ternary azeotrope is present. The data were correlated by the Redlich-Kister, Van Laar, Wilson and Wisniak-Tamir equations and the appropriate parameters are reported. The activity coefficients of the ternary system can be predicted from those of the pertinent binary systems.

KEY WORDS: Activity coefficients, vapor-liquid equilibrium

The present work was undertaken to measure vapor-liquid equilibria (VLE) data for the title systems for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for organic halides. Data for the binary system 2-chlorobutane + 1-chlorobutane have already been reported (1).

EXPERIMENTAL

Purity of Materials

2-chlorobutane (99.9 mole % +), 1-chlorobutane (99.84 mole% +) and cyclohexane (99.9 mole % +) were purchased from Merck. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties and purity (as determined by glc) of the pure components appear in Table 1.

Apparatus and Procedure

An all-glass modified Dvorak and Boublik recirculation still (2) was used in the VLE measurements. The experimental features have been described in a previous

Table 1 Mole % GLC purities, refractive index n_D at Na D line, and normal boiling points T of pure components

Component (Purity, mole %)	$n_D(298.15\,K)$	T/K
2-Chlorobutane (99.9)	1.3941[a]	341.24[a]
	1.3941[b]	341.25[b]
1-Chlorobutane (99.84)	1.3999[a]	351.58[a]
	1.4000[b]	351.58[b]
Cyclohexane (99.9)	1.4233[a]	353.82[a]
	1.42354[b]	353.88[b]

[a]Measured
[b]Reference 12

publication (3). All analyses were carried out by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 2 m long and 0.2 cm in diameter, filled with SE-30, the column and detector temperatures were 323.15 K and 523.15 K respectively; the injector temperature was 493.15 K for the ternary system and the binary 1-chlorobutane + cyclohexane, and 523.15 for the binary system 2-chlorobutane + cyclohexane. Very good separation was achieved under these conditions, and calibration analyses with gravimetrically prepared samples were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ± 0.008 mole fraction units. The accuracy in determination of pressure P and temperature T was at least ± 0.1 kPa and 0.02 K, respectively.

RESULTS

The temperature t, liquid-phase x_i, and vapor-phase y_i mole fraction measurements at $P = 101.3$ kPa are reported in Tables 2–4 and Figures 1–3, together with the activity coefficients γ_i which were calculated from the following Eq. (4):

$$\ln \gamma_i = \ln(Py_i/P_i^0 x_i) + (B_{ii} - v_i^L)(P - P_i^0)/RT + (P/2RT)\sum_1^n \sum_1^n y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where:

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation:

$$\log(P_i^0/\text{kPa}) = A_i - B_i/(T/K - C_i) \quad (3)$$

where the constants A_i, B_i, C_i are reported in Table 5. The molar virial coefficients B_{ii}, and B_{ij} were estimated by the method of O'Connell and Prausnitz (5) using the

Table 2 Experimental vapor-liquid equilibrium data for 2-chlorobutane (1) + cyclohexane(3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3	$-B_{11}$ ($cm^3\,mol^{-1}$)	$-B_{33}$ ($cm^3\,mol^{-1}$)	$-B_{13}$ ($cm^3\,mol^{-1}$)
351.42	0.071	0.131	1.3744	1.0048	1025	1129	1079
350.59	0.102	0.174	1.3006	1.0125	1031	1136	1085
349.40	0.155	0.239	1.2157	1.0269	1040	1145	1095
347.75	0.236	0.340	1.1905	1.0348	1053	1159	1108
347.16	0.271	0.369	1.1444	1.0555	1057	1163	1112
345.94	0.352	0.456	1.1278	1.0623	1067	1174	1122
345.11	0.421	0.514	1.0889	1.0894	1073	1181	1129
344.45	0.479	0.562	1.0668	1.1135	1079	1186	1135
344.20	0.503	0.589	1.0725	1.1037	1081	1188	1137
343.17	0.614	0.678	1.0426	1.1495	1089	1197	1145
342.74	0.673	0.721	1.0245	1.1915	1092	1201	1149
342.36	0.728	0.766	1.0176	1.2158	1096	1204	1152
342.10	0.779	0.807	1.0097	1.2442	1098	1207	1154
341.77	0.843	0.860	1.0041	1.2837	1100	1209	1157
341.54	0.888	0.899	1.0034	1.3076	1102	1211	1159
341.38	0.931	0.936	1.0012	1.3517	1104	1213	1160

Table 3 Experimental vapor-liquid equilibrium data for 1-chlorobutane (2) + cyclohexane (3) at 101.3 kPa

T/K	x_1	y_2	γ_2	γ_3	$-B_{22}$ ($cm^3\,mol^{-1}$)	$-B_{33}$ ($cm^3\,mol^{-1}$)	$-B_{23}$ ($cm^3\,mol^{-1}$)
353.16	0.043	0.061	1.3542	1.0019	1154	1116	1134
352.46	0.092	0.124	1.3133	1.0054	1159	1121	1139
351.84	0.151	0.187	1.2289	1.0161	1164	1126	1144
351.12	0.235	0.278	1.1992	1.0228	1170	1132	1150
350.69	0.305	0.342	1.1514	1.0391	1173	1135	1153
350.44	0.368	0.395	1.1104	1.0584	1176	1137	1155
350.26	0.418	0.441	1.0973	1.0676	1177	1138	1157
350.09	0.488	0.500	1.0711	1.0910	1178	1140	1158
350.00	0.539	0.545	1.0598	1.1055	1179	1140	1159
350.01	0.611	0.607	1.0410	1.1313	1179	1140	1159
350.05	0.652	0.644	1.0338	1.1442	1179	1140	1159
350.21	0.740	0.725	1.0205	1.1774	1177	1139	1157
350.41	0.801	0.782	1.0108	1.2123	1176	1137	1156
350.65	0.860	0.842	1.0064	1.2401	1174	1135	1154
351.00	0.920	0.904	0.9997	1.3051	1171	1133	1151
351.20	0.951	0.939	0.9986	1.3460	1169	1131	1149

molecular parameters suggested by the authors and assuming the association parameter eta to be zero. The last two terms in equation 1 contributed less than 3% to the activity coefficient and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2–4 and are estimated accurate to within $\pm 3\%$.

The binary data reported in Tables 2 and 3 were found to be thermodynamically consistent by the Herington criteria (6) and the L-W method of Wisniak (7). The ternary activity coefficients were found to be thermodynamically consistent as tested

Table 4 Experimental vapor-liquid equilibria data for 2-chlorobutane (1) + 1-chlorobutane (2) + cyclohexane (3) at 101.3 kPa

					Activity coefficients								
								$-B_{12}$	$-B_{13}$	$-B_{23}$	$-B_{11}$	$-B_{22}$	$-B_{33}$
T/k	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$cm^3\,mol^{-1}$					
341.69	0.906	0.040	0.920	0.030	1.0066	1.0155	1.3362	1101	1250	1210	1175	1158	1229
341.82	0.883	0.050	0.902	0.037	1.0086	0.9979	1.3085	1100	1249	1209	1174	1157	1228
342.04	0.852	0.063	0.873	0.048	1.0056	1.0203	1.3182	1098	1247	1207	1172	1155	1226
342.05	0.879	0.089	0.901	0.068	1.0056	1.0210	1.3611	1098	1247	1207	1172	1155	1226
342.27	0.809	0.081	0.838	0.062	1.0090	1.0176	1.2883	1096	1245	1205	1170	1153	1224
342.42	0.729	0.032	0.766	0.025	1.0188	1.0337	1.2335	1095	1244	1204	1169	1152	1223
342.59	0.760	0.101	0.796	0.078	1.0104	1.0164	1.2718	1094	1242	1202	1167	1150	1221
342.93	0.709	0.122	0.749	0.097	1.0094	1.0353	1.2613	1091	1239	1199	1164	1147	1218
342.96	0.726	0.147	0.770	0.112	1.0118	0.9945	1.2836	1091	1239	1199	1164	1147	1218
343.11	0.736	0.191	0.786	0.146	1.0142	0.9897	1.2859	1089	1238	1198	1163	1146	1217
343.14	0.722	0.179	0.767	0.139	1.0080	1.0045	1.3095	1089	1237	1197	1162	1145	1217
343.21	0.642	0.084	0.689	0.068	1.0161	1.0448	1.2205	1089	1237	1197	1162	1145	1216
343.34	0.644	0.111	0.693	0.091	1.0149	1.0538	1.2084	1088	1236	1196	1161	1144	1215
343.36	0.646	0.129	0.693	0.104	1.0112	1.0357	1.2359	1087	1235	1196	1161	1144	1215
343.51	0.581	0.027	0.645	0.021	1.0417	0.9945	1.1617	1086	1234	1194	1159	1142	1213
343.52	0.647	0.188	0.704	0.146	1.0207	0.9926	1.2391	1086	1234	1194	1159	1142	1213
343.70	0.670	0.222	0.718	0.178	0.9999	1.0191	1.3052	1085	1232	1193	1158	1141	1212
343.93	0.545	0.108	0.605	0.090	1.0295	1.0565	1.1793	1083	1230	1191	1156	1139	1210
344.00	0.554	0.139	0.618	0.112	1.0316	1.0137	1.1816	1082	1230	1190	1155	1138	1209
344.10	0.658	0.315	0.710	0.263	0.9948	1.0480	1.3388	1081	1229	1189	1154	1137	1208
344.25	0.515	0.168	0.571	0.143	1.0176	1.0635	1.2023	1080	1228	1188	1153	1136	1207
344.53	0.511	0.260	0.579	0.212	1.0313	1.0099	1.2058	1078	1225	1186	1151	1134	1204
344.59	0.563	0.295	0.628	0.237	1.0135	0.9932	1.2537	1078	1225	1185	1150	1133	1204
344.60	0.464	0.021	0.545	0.018	1.0669	1.0594	1.1187	1077	1225	1185	1150	1133	1204
344.79	0.456	0.049	0.537	0.044	1.0625	1.0921	1.1117	1076	1223	1183	1149	1132	1202
344.81	0.448	0.079	0.526	0.069	1.0608	1.0793	1.1190	1076	1223	1183	1148	1132	1202
344.98	0.454	0.251	0.524	0.208	1.0366	1.0122	1.1838	1074	1221	1182	1147	1130	1201
345.27	0.508	0.407	0.577	0.337	1.0114	1.0023	1.3067	1072	1219	1179	1145	1128	1198
345.30	0.407	0.202	0.471	0.178	1.0295	1.0657	1.1583	1072	1218	1179	1144	1128	1198
345.42	0.392	0.185	0.465	0163	1.0505	1.0588	1.1335	1071	1217	1178	1143	1127	1197
345.48	0.455	0.371	0.521	0.310	1.0133	1.0049	1.2463	1070	1217	1177	1143	1126	1196
345.54	0.382	0.073	0.465	0.067	1.0755	1.0943	1.1011	1070	1216	1177	1142	1126	1196

345.71	0.502	0.476	0.575	0.403	1.0068	1.0110	1.2742	1069	1215	1176	1141	1124	1194
345.75	0.400	0.387	0.463	0.330	1.0162	1.0170	1.2368	1068	1215	1175	1141	1124	1194
346.01	0.343	0.276	0.405	0.247	1.0287	1.0589	1.1533	1066	1212	1173	1139	1122	1192
346.03	0.351	0.263	0.417	0.232	1.0344	1.0431	1.1475	1066	1212	1173	1138	1122	1192
346.13	0.415	0.485	0.482	0.416	1.0083	1.0111	1.2832	1065	1211	1172	1138	1121	1191
346.16	0.383	0.449	0.447	0.386	1.0123	1.0125	1.2494	1065	1211	1172	1137	1121	1191
346.24	0.444	0.515	0.517	0.440	1.0076	1.0037	1.3150	1065	1210	1171	1137	1120	1190
346.37	0.335	0.060	0.424	0.056	1.0927	1.0922	1.0726	1064	1209	1170	1136	1119	1189
346.38	0.312	0.130	0.394	0.120	1.0900	1.0799	1.0865	1063	1209	1170	1135	1119	1189
346.47	0.294	0.352	0.361	0.311	1.0554	1.0307	1.1537	1063	1208	1169	1135	1118	1188
346.65	0.294	0.064	0.393	0.063	1.1429	1.1511	1.0485	1061	1207	1168	1133	1117	1186
346.69	0.278	0.207	0.345	0.194	1.0632	1.0862	1.1047	1061	1207	1167	1133	1116	1186
346.72	0.273	0.228	0.338	0.213	1.0545	1.0865	1.1107	1061	1206	1167	1133	1116	1186
346.76	0.387	0.548	0.456	0.474	1.0055	1.0001	1.3190	1060	1206	1167	1132	1116	1186
346.78	0.272	0.274	0.334	0.230	1.0497	1.0761	1.1158	1060	1206	1167	1132	1115	1185
346.84	0.269	0.304	0.326	0.288	1.0339	1.0928	1.1103	1060	1205	1166	1132	1115	1185
347.05	0.239	0.349	0.301	0.319	1.0643	1.0491	1.1270	1058	1204	1164	1130	1113	1183
347.14	0.258	0.184	0.329	0.174	1.0748	1.0807	1.0868	1058	1203	1164	1129	1113	1182
347.16	0.256	0.462	0.305	0.420	1.0036	1.0384	1.1891	1057	1203	1163	1129	1112	1182
347.17	0.231	0.279	0.299	0.262	1.0876	1.0703	1.0945	1057	1203	1163	1129	1112	1182
347.33	0.292	0.602	0.353	0.534	1.0133	1.0080	1.2932	1056	1201	1162	1128	1111	1181
347.41	0.222	0.452	0.275	0.410	1.0355	1.0271	1.1730	1055	1201	1161	1127	1110	1180
347.45	0.236	0.494	0.290	0.444	1.0242	1.0188	1.1908	1055	1200	1161	1127	1110	1180
347.65	0.199	0.242	0.259	0.235	1.0808	1.0928	1.0876	1054	1199	1159	1125	1109	1178
347.69	0.305	0.642	0.368	0.575	1.0008	1.0067	1.2906	1053	1198	1159	1125	1108	1178
347.70	0.187	0.392	0.240	0.365	1.0642	1.0463	1.1256	1053	1198	1159	1125	1108	1178
347.75	0.252	0.620	0.310	0.555	1.0186	1.0043	1.2634	1053	1198	1159	1124	1108	1177
347.89	0.180	0.217	0.247	0.216	1.1316	1.1121	1.0623	1052	1197	1158	1123	1107	1176
347.93	0.201	0.578	0.240	0.534	0.9835	1.0309	1.2184	1051	1196	1157	1123	1106	1176
348.00	0.203	0.611	0.247	0.562	1.0002	1.0242	1.2209	1051	1196	1157	1122	1106	1175
348.02	0.187	0.134	0.254	0.139	1.1158	1.1458	1.0638	1051	1195	1156	1122	1106	1175
348.10	0.152	0.307	0.204	0.301	1.1000	1.0884	1.0846	1050	1195	1156	1122	1105	1174
348.20	0.139	0.350	0.187	0.340	1.0995	1.0751	1.0939	1049	1194	1155	1121	1104	1174
348.38	0.243	0.720	0.292	0.668	0.9770	1.0212	1.2707	1048	1192	1154	1119	1103	1172
348.46	0.135	0.292	0.180	0.291	1.0815	1.0943	1.0826	1047	1192	1153	1119	1102	1171
348.60	0.111	0.515	0.143	0.491	1.0408	1.0425	1.1428	1046	1191	1152	1118	1101	1170
348.66	0.112	0.344	0.149	0.344	1.0729	1.0915	1.0864	1046	1190	1151	1117	1101	1170

Table 4 (*Contd.*)

Activity coefficients													
								$-B_{12}$	$-B_{13}$	$-B_{23}$	$-B_{11}$	$-B_{22}$	$-B_{33}$
T/k	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$cm^3\,mol^{-1}$					
348.75	0.105	0.520	0.136	0.497	1.0469	1.0404	1.1362	1045	1189	1151	1116	1100	1169
348.83	0.157	0.101	0.228	0.109	1.1654	1.1720	1.0363	1045	1189	1150	1116	1099	1168
348.89	0.142	0.697	0.174	0.657	0.9817	1.0217	1.2152	1044	1188	1149	1115	1099	1168
349.00	0.125	0.153	0.188	0.167	1.2011	1.1793	1.0308	1043	1187	1148	1114	1098	1167
349.05	0.082	0.566	0.106	0.541	1.0421	1.0329	1.1489	1043	1187	1148	1114	1097	1167
349.48	0.108	0.771	0.134	0.735	0.9773	1.0152	1.2315	1040	1183	1145	1111	1094	1163
349.49	0.041	0.479	0.057	0.479	1.0947	1.0646	1.0993	1040	1183	1145	1111	1094	1163
349.53	0.062	0.719	0.082	0.686	1.0257	1.0145	1.2086	1039	1183	1114	1110	1094	1163
349.59	0.122	0.078	0.185	0.090	1.1906	1.2247	1.0275	1039	1182	1144	1110	1093	1162
349.67	0.054	0.319	0.079	0.338	1.1494	1.1203	1.0527	1038	1182	1143	1109	1093	1162
349.68	0.025	0.444	0.036	0.456	1.1210	1.0859	1.0828	1038	1182	1143	1109	1093	1162
349.72	0.056	0.274	0.081	0.297	1.1314	1.1460	1.0485	1038	1181	1143	1109	1092	1161
349.89	0.084	0.821	0.106	0.789	0.9824	1.0109	1.2421	1037	1180	1141	1107	1091	1160
349.96	0.047	0.789	0.062	0.757	1.0223	1.0071	1.2381	1036	1179	1141	1107	1090	1159
345.00	0.089	0.108	0.143	0.126	1.2468	1.2289	1.0190	1036	1179	1140	1107	1090	1159
350.06	0.031	0.328	0.045	0.349	1.1245	1.1136	1.0571	1035	1179	1140	1106	1090	1159
350.14	0.065	0.178	0.101	0.203	1.2010	1.1908	1.0256	1035	1178	1139	1105	1089	1158
350.23	0.068	0.855	0.086	0.828	0.9766	1.0084	1.2417	1034	1177	1139	1105	1088	1157
350.58	0.068	0.083	0.116	0.101	1.2964	1.2679	1.0149	1031	1174	1136	1102	1086	1154
350.62	0.037	0.182	0.059	0.215	1.2157	1.2159	1.0223	1031	1174	1136	1102	1085	1154
350.95	0.076	0.038	0.132	0.047	1.3118	1.2607	1.0092	1029	1171	1133	1099	1083	1151

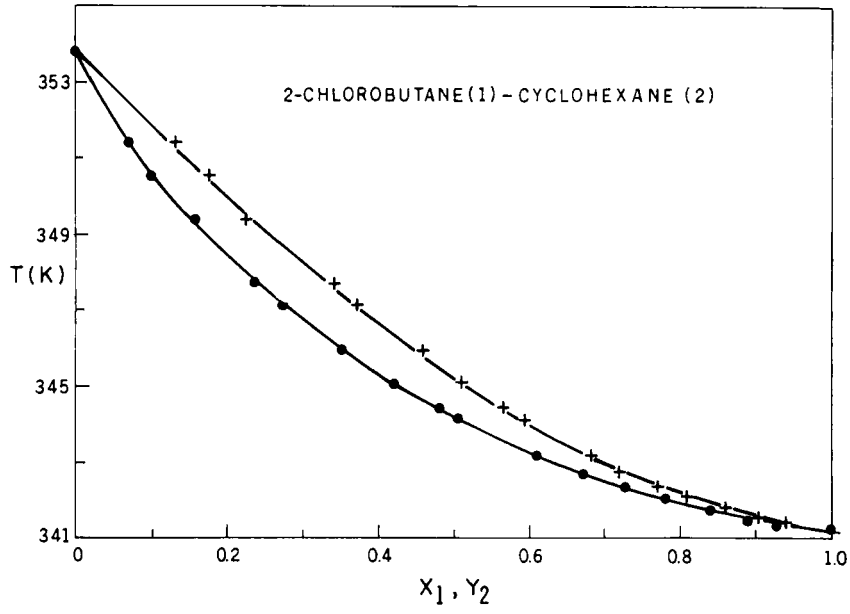

Figure 1 Boiling temperature diagram for the system 2-chlorobutane (1)–cyclohexane (2) at 101.3 kPa.

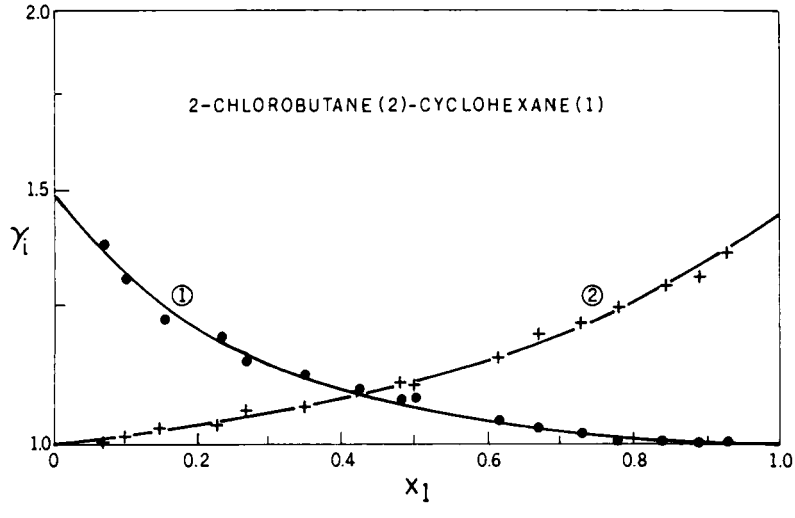

Figure 2 Activity coefficients for the system 2-chlorobutane (1)–cyclohexane (2) at 101.3 kPa.

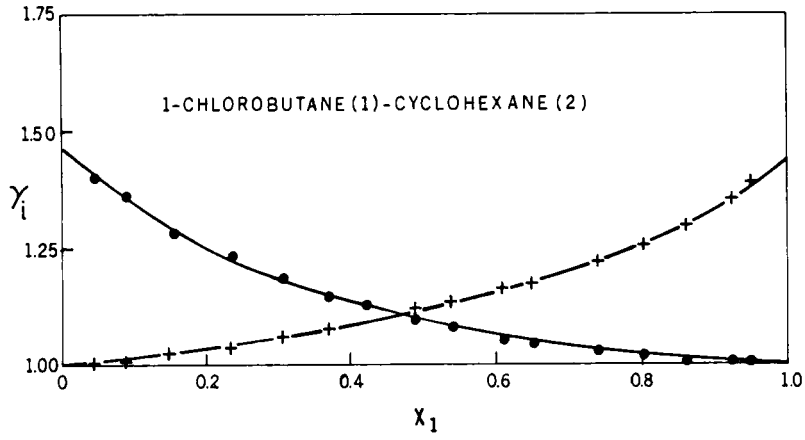

Figure 3 Activity coefficients for the system 1-chlorobutane (1)–cyclohexane (2) at 101.3 kPa.

Table 5 Antoine coefficients, Eq. 3

compound	A_i	B_i	C_i
2-chlorobutane[1]	6.12220	1245.2	38.75
1-chlorobutane[1]	6.05154	1216.82	50.82
cyclohexane[1]	5.96407	1200.31	50.65

[1]Reference 12

by the L-W method of Wisniak (7) and the McDermot-Ellis method (8) modified by Wisniak and Tamir (9). For the latter the values of D_{max} were at least 0.373 while the values of D for any given point never exceeded 0.030. The McDermot-Ellis test requires that $D < D_{max}$ for every point.

The excess Gibbs function of the two binary systems are presented in Table 6 and Figure 4 as the variation of the dimensionless number (Gibbs number) $\Delta G^E/RT$ with composition. The values of the parameter are positive over the entire composition range, the value at $x = 0.5$ for the binary 2-chlorobutane-cyclohexane is larger than that for the binary 1-chlorobutane-cyclohexane probably due to the larger steric influence.

The activity coefficients for the 2-chlorobutane-cyclohexane and 1-chlorobutane-cyclohexane binaries were correlated by the Redlich-Kister (a), Van Laar (b) and Wilson (c) models (10):

$$\text{(a) } \log \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(10x_1x_2 - 1) \tag{4}$$

$$\text{(b) } \log \gamma_1 = A\left[\frac{Bx_2}{Ax_1 + Bx_2}\right]^2 \quad \log \gamma_2 = B\left[\frac{Ax_1}{Ax_1 + Bx_2}\right]^2 \tag{5}$$

Table 6 Variation of $\Delta G^E/RT$ with composition

2-chlorobutane + cyclohexane		*1-chlorobutane + cyclohexane*	
x_1	$\Delta G^E/RT$	x_1	$\Delta G^E/RT$
0.000	0.0000	0.000	0.0000
0.071	0.0271	0.043	0.0149
0.102	0.0379	0.092	0.0299
0.155	0.0527	0.151	0.0447
0.236	0.0673	0.235	0.0599
0.271	0.0759	0.305	0.0696
0.352	0.0815	0.368	0.0744
0.421	0.0854	0.418	0.0769
0.479	0.0870	0.488	0.0781
0.503	0.0843	0.539	0.0776
0.614	00794	0.611	0.0725
0.673	0.0736	0.652	0.0685
0.728	0.0658	0.740	0.0575
0.779	0.0558	0.801	0.0469
0.843	0.0449	0.860	0.0357
0.888	0.0316	0.920	0.0210
0.931	0.0219	0.951	0.0132
1.000	0.0000	1.000	0.0000

$$\text{(c)}\quad \ln \gamma_1 = -\ln(x_1 + Ax_2) + x_2\left(\frac{A}{x_1 + Ax_2} - \frac{B}{x_2 + Bx_1}\right)$$

$$\ln \gamma_2 = -\ln(x_2 + Bx_1) - x_1\left(\frac{A}{x_1 + Ax_2} - \frac{B}{x_2 + Bx_1}\right) \tag{6}$$

The values of the pertinent parameters and statistics appear in Table 7.

The activity coefficients for the ternary system were correlated by the following Redlich-Kister expansion (10):

$$\begin{aligned}\ln \gamma_1/\gamma_2 = {} & b_{12}(x_2 - x_1) - c_{12}[(x_1 - x_2)^2 - 2x_1x_2] \\ & + d_{12}(x_2 - x_1)[(x_1 - x_2)^2 - 4x_1x_2] + x_3[b_{13} + c_{13}(2x_1 - x_3) \\ & + d_{13}(x_1 - x_3)(3x_1 - x_3) - b_{23} - c_{23}(2x_2 - x_3) \\ & - d_{23}(x_2 - x_3)(3x_2 - x_3) + C_1(x_2 - x_1)]\end{aligned} \tag{7}$$

where b_{ij}, c_{ij} and d_{ij} are constants for the pertinent binary and C_1 is a ternary constant. The equations for two other pair of activity coefficients were obtained by cyclic rotation of the indices. The binary system 2-chlorobutane + 1-chlorobutane behaves essentially ideally and has been reported elsewhere (1). The ternary Redlich-Kister coefficient was obtained by a Simplex optimization technique. The differences between the values of the root mean square deviation for the activity coefficient for the two cases – with and without the ternary constant C_1 (Table 8) – are statistically not significant suggesting that ternary data can be predicted directly from the binary systems.

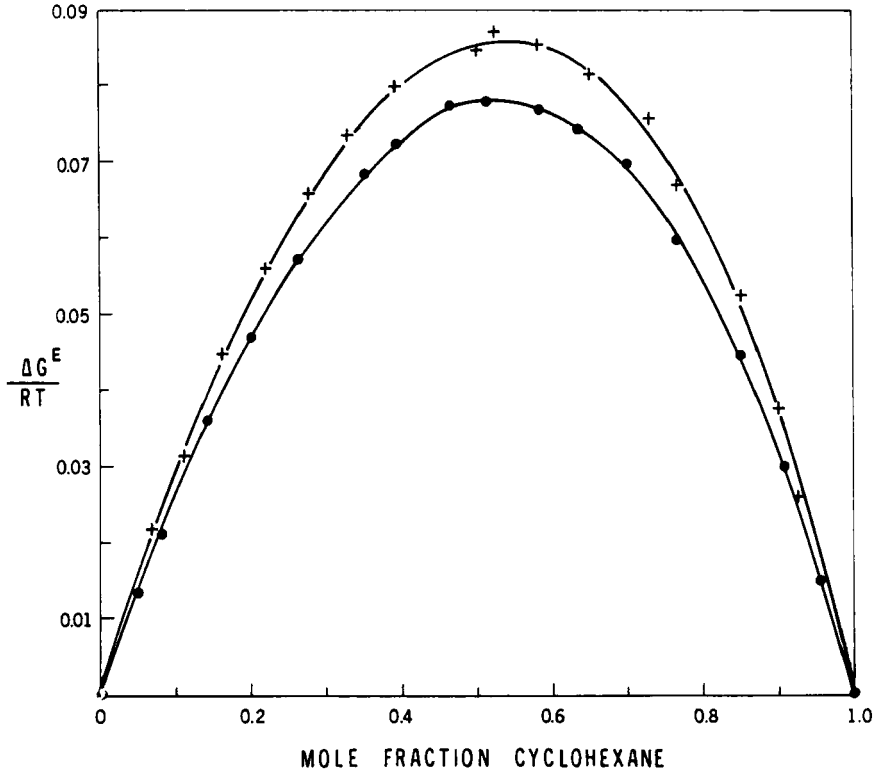

Figure 4 Variation of $\Delta G^E/RT$ with composition for 2-chlorobutane + cyclohexane (+) and 1-chlorobutane-cyclohexane (o).

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (11):

$$T/K = \sum_{i=1}^{n} x_i T_i^0/K + \sum_{i,j=1}^{n} \left\{ x_i x_j \sum_{k=0}^{l} C_k (x_i - x_j)^k \right\} + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (8)$$

In these equations n is the number of components ($n = 2$ or 3), T_i^0 is the boiling point of the pure component l (in K or $°C$) and i is the number of terms in the series expansion of $(x_i - x_j)$. C_k are the binary constants where A, B, C, D are ternary constants. An equation of the same structure can be used for the direct correlation of ternary data, without use of binary data. Both forms will require about the same number of constants for similar accuracy but the direct correlation allows an easier calculation of boiling isotherms (Fig. 5). The various constants of Eq. 8 are reported in Table 9, which also contains information indicating the degree of goodness of the correlation.

Table 7 Coefficients for the different models, Eqs. 4–6.

Model	*Redlich-Kister*				*Van Laar*			*Wilson*		
System	*B*	*C*	*D*	*rmsd*	*A*	*B*	*rmsd*	*A*	*B*	*rmsd*
2-chlorobutane (1) + cyclohexane (3)	0.1407	−0.0188	0.0193	0.01	0.15680	0.14463	0.004	0.58200	1.13067	0.008
1-chlorobutane (2)	0.1320	−0.0085	0.160	0.003	0.15733	0.12170	0.004	0.65499	1.06633	0.003

Table 8 Redlich-Kister Coefficients, Eq. 7
Ternary System

	b_{12}	c_{12}	d_{12}	b_{13}	c_{13}	d_{13}	b_{23}	c_{23}	d_{23}	C_1	*rmsd* γ_1/γ_2	*rmsd* γ_1/γ_3
2-chlorobutane + 1-chlorobutane (2) + cyclohexane (3)	0	0	0	0.1407	−0.0188	0.0193	0.1320	−0.0085	0.0160	0	0.003	0.002
										−0.02598	0.003	0.002

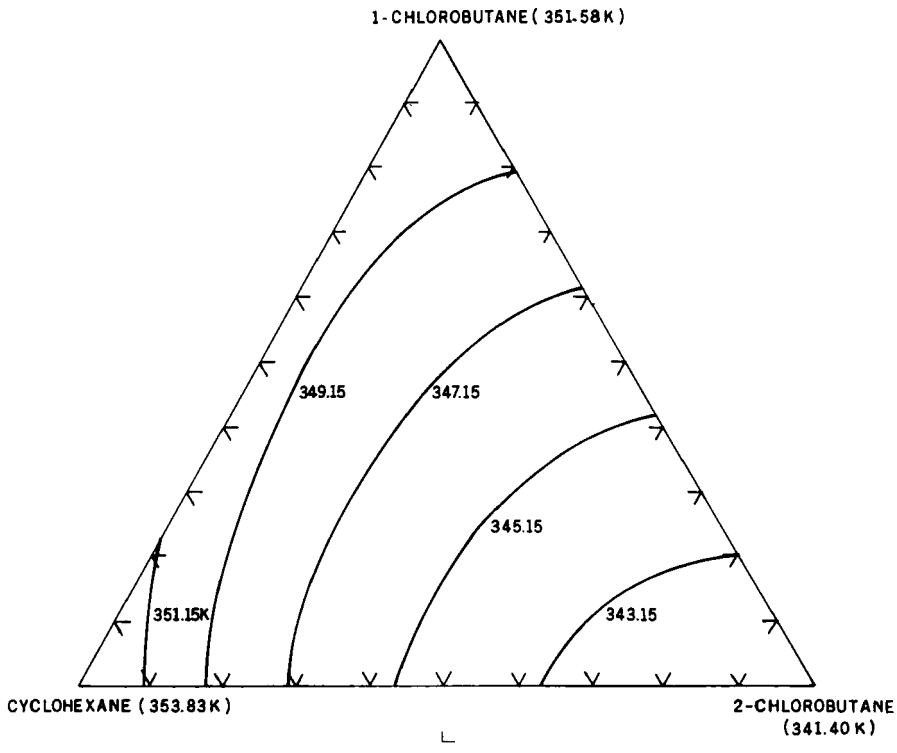

Figure 5 Isothermals for the ternary system 2-chlorobutane–1-chlorobutane–cyclohexane at 101.3 kPa. Coefficients from Eq. 6.

Table 9 Coefficients in correlation of boiling points, Eq. 8 and root mean square deviations in temperature, rmsd (T/K)

System	C_0	C_1	C_2	*rmsd*	%[1]
2-Chlorobutane (1) + 1-chlorobutane (2)	−1.8554	0.5540	0	0.01	0.04
2-Chlorobutane (1) + cyclohexane (3)	−10.538	1.9321	−2.1549	0.01	0.01
1-Chlorobutane (2) + cyclohexane (3)[2]	−35.530	−11.723	−19.298	0.01	0.06
	A	*B*	*C*	*rmsd*	
2-Chlorobutane (1) + 1-Chlorobutane (2) + cyclohexane (3)	−8.2473	27.3254	—	0.03	

[1]Average % deviation
[2]Reference 1

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GLOSSARY

A_i, B_i, C_i	Antoine constants, Eq 3
B_{ii}, B_{ij}	second molar virial coefficients, Eqs 1,2
b_{ii}, c_{ij}, d_{ii}	Redlich-Kister constants, Eq 4
C_k	constants, Eq 5
ΔG^E	excess Gibbs function
N	number of measurements
P	total pressure
P_i^0	vapor pressure of pure components i
R	gas constant
rmsd (T)	root mean square deviation, $\{\Sigma(T_{expt} - T_{calc})^2\}^{0.5}/N$
rmsd (γ_i)	root mean square deviation, $\{\Sigma(\gamma_{iexpt} - \gamma_{icalc})^2\}^{0.5}/N$
t, T	boiling temperature of a mixture
t_i^0	boiling temperature of pure component i
v_i^L	molar volume of liquid component i
x_i, y_i	mole fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i
δ_{ij}	molar virial coefficient parameter, Eq. 2

Subscripts

expt	experimental value
calc	calculated value
i	component i