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Vapor−Liquid Equilibria in the Ternary System Hexane + 1-Chlorobutane + 2-Propanol and Its Binaries

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Vapor−liquid equilibrium at 94.4 kPa has been determined for the ternary system hexane + 1-chlorobutane + 2-propanol and the binary systems hexane + 1-chlorobutane and 1-chlorobutane + 2-propanol. The binary system hexane + 1-chlorobutane exhibits moderate deviations from ideality and an azeotrope that contains 97.5 mol % hexane and boils at 339.25 K. The binary system 1-chlorobutane + 2-propanol presents strong deviations from ideality and an azeotrope that contains 62.8 mol % 1-chlorobutane and boils at 341.60 K. The equilibrium data were correlated by the Redlich−Kister, Wilson, UNIQUAC, UNIFAC, and Wisniak−Tamir equations, and the appropriate parameters are reported. The activity coefficients of the ternary system are predicted from those of the pertinent binary systems very well by the Wilson equation and not so well by the Redlich−Kister equation. A ternary azeotrope is not present.

The present work was undertaken to measure vapor−liquid equilibrium (VLE) data for the title systems for which no isobaric data are available. Data for the binary system hexane + 2-propanol have already been reported at 94.4 kPa (Wisniak and Akunis, 1995); this system exhibits large positive deviations from ideal behavior and an azeotrope that boils at 332.92 K and contains 73.3 mol % hexane. Gutsche and Knapp (1982) have measured the vapor−liquid equilibria for the system 1-chlorobutane + hexane at 300, 325, and 350 K. The ternary system in question is of interest because each of the three binary subsystems presents an azeotrope and the presence of associating effects of the alcohol. Mixtures of alcohols and saturated hydrocarbons are complex because the degree of alcohol bonding is strongly dependent on the composition. The theory of alcohol−hydrocarbon solutions is well documented in the literature (Scatchard, 1949; Kretschmer and Wiebe, 1954; Renon and Prausnitz, 1967).

Experimental Section

Purity of Materials. Hexane (99.5+ mol %) was purchased from Phillips, 1-chlorobutane (99.9+ mol %) from Merck, and 2-propanol (99.6+ mol %) from Frutarom. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purities (as determined by GLC) of the pure components appear in Table 1.

Apparatus and Procedure. An all glass vapor−liquid equilibrium apparatus, model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, the solution is heated to its boiling point by a 250 W immersion heater. The vapor−liquid mixture flows through an extended contact line which guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and return again to the immersion heater. Temperature control is achieved by a 5 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.1 K. The total pressure P of the system is controlled by a vacuum pump capable of working under vacuum up to 0.25 kPa. The pressure is measured by a Vac Probs with an accuracy of ±0.1 kPa. On average the system reaches equilibrium conditions after 1−2 h of operation.

Table 1. Mole Percent GLC Purities, Refractive Index n_D at the Na D Line, Normal Boiling Points T, and Liquid Molar Volumes of the Pure Components

component (purity (mol %))	n_D(298.15 K)	T/K	v_i^L/(cm^3·mol^{-1})^b
hexane (99.5)	1.3731^a	341.84^a	
	1.3723^b	341.89^b	133.80
1-chlorobutane (99.9)	1.4000^a	351.58^a	
	1.4000^b	351.58^b	72.96
2-propanol (99.6)	1.3752^a	355.50^a	
	1.3752^b	355.41^b	76.92

^{a} Measured. ^{b} TRC (1974).

Samples, taken by syringing 0.7 μL after the system had achieved equilibrium, were analyzed 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 and filled with 10% SE-30, the temperatures of the column, injector, and detector were 323.15, 493.15, and 523.15 K, respectively, for the three binaries and 318.15, 403.15, and 543.15 K for the ternary system. Very good separation was achieved under these conditions, and calibration analyses with gravimetrically prepared samples were carried out to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±0.008 mole fraction unit. The accuracies in determination of pressure the P and temperature T were at least ±0.1 kPa and ±0.1 K, respectively.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at P = 94.4 kPa are reported in Tables 2−4 and Figures 1−4, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

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

where B_{ii} and B_{jj} are the second virial coefficients of the

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Table 2. Experimental Vapor–Liquid Equilibrium Data for Hexane (1) + 1-Chlorobutane (2) at 94.4 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ ($cm^3 \cdot mol^{-1}$)	$-B_{22}$/ ($cm^3 \cdot mol^{-1}$)	$-B_{12}$/ ($cm^3 \cdot mol^{-1}$)	G^E/RT
349.25	0	0		1			0	
348.25	0.031	0.054	1.3610	1.0079	1263	1196	1234	0.017
347.75	0.047	0.080	1.3604	1.0112	1267	1200	1238	0.025
347.15	0.072	0.121	1.3464	1.0112	1273	1205	1244	0.032
346.15	0.124	0.193	1.2835	1.0144	1282	1214	1253	0.044
344.95	0.186	0.273	1.2553	1.0202	1293	1224	1263	0.059
343.65	0.272	0.366	1.1959	1.0357	1306	1236	1275	0.074
342.55	0.332	0.433	1.1932	1.0470	1316	1245	1286	0.089
342.65	0.347	0.444	1.1665	1.0473	1316	1244	1285	0.084
341.45	0.466	0.553	1.1234	1.0684	1327	1255	1296	0.090
340.95	0.494	0.566	1.1016	1.1116	1332	1260	1301	0.101
339.85	0.678	0.718	1.0534	1.1734	1343	1270	1311	0.087
339.35	0.800	0.816	1.0290	1.2564	1348	1274	1316	0.069
339.35	0.86	0.868	1.0183	1.2869	1348	1274	1316	0.051
339.15	0.922	0.925	1.0183	1.3226	1350	1276	1318	0.039
339.25	0.929	0.932	1.0145	1.3245	1349	1275	1317	0.033
339.25	0.952	0.953	1.0133	1.3352	1349	1275	1317	0.026
339.25	0.969	0.970	1.0126	1.3427	1349	1275	1317	0.021
339.25	0.975	0.975	1.0123	1.3527	1349	1275	1317	0.020
339.35	0.988	0.987	1.0082	1.4436	1348	1274	1316	0.013
339.60	1	1	1					0
$\gamma_i^{\infty\,a}$			1.438	1.470				

[a] Calculated according to Wisniak et al. (1995).

Table 3. Experimental Vapor–Liquid Equilibrium Data for 1-Chlorobutane (1) + 2-Propanol (2) at 94.4 kPa

T/ K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ ($cm^3 \cdot mol^{-1}$)	$-B_{22}$/ ($cm^3 \cdot mol^{-1}$)	$-B_{12}$/ ($cm^3 \cdot mol^{-1}$)	G^E/RT
353.45	0	0		1				0
349.85	0.058	0.185	3.1537	1.0069	665	719	733	0.073
348.65	0.081	0.241	3.0214	1.0096	670	727	741	0.098
348.15	0.092	0.263	2.9643	1.0125	673	730	744	0.111
347.35	0.118	0.299	2.6909	1.0246	677	735	749	0.138
345.75	0.177	0.381	2.3994	1.0364	684	746	759	0.184
344.15	0.223	0.442	2.3232	1.0580	693	758	770	0.232
342.95	0.296	0.495	2.0439	1.1097	699	766	778	0.285
342.05	0.391	0.546	1.7531	1.2002	703	773	785	0.331
341.85	0.498	0.586	1.4864	1.3394	704	774	786	0.344
341.65	0.553	0.605	1.3911	1.4476	706	776	787	0.348
341.55	0.654	0.639	1.2466	1.7167	706	777	788	0.331
341.65	0.672	0.647	1.2247	1.7626	706	776	787	0.322
342.55	0.829	0.718	1.0705	2.5993	701	769	781	0.220
343.85	0.920	0.797	1.0278	3.7767	694	760	772	0.132
345.05	0.943	0.845	1.0228	3.8549	688	751	764	0.098
345.35	0.949	0.853	1.0157	4.0699	686	749	762	0.086
346.95	0.977	0.922	1.0154	4.4312	679	738	752	0.049
349.25	1	1	1					0
$\gamma_i^{\infty\,a}$			3.954	6.503				

[a] Calculated according to Wisniak et al. (1995).

pure components, B_{ij} is the cross second virial coefficient, v_i^L is the liquid molar volume of pure component i, R is the universal gas constant, and

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

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 $P_i°$ were calculated according to the Antoine equation:

$$\log(P_i°/\text{kPa}) = A_i - B_i/(T/\text{K} - C_i) \qquad (3)$$

The Antoine constants A_i, B_i, and 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 (1967) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in eq 1 contributed less than 2% 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 ±3%. Tables 2 and 3 also report the values for the activity coefficients at infinite dilution, calculated using the weighted volatility function as proposed by Wisniak et al. (1995).

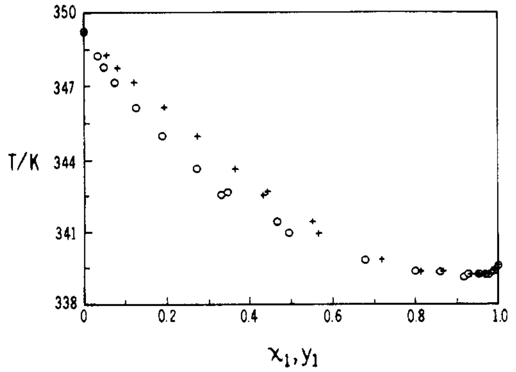

Figure 1. Boiling point diagram at 94.4 kPa for the system hexane (1) + 1-chlorobutane (2).

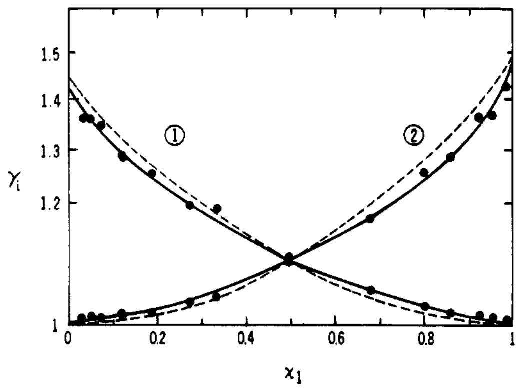

Figure 2. Activity coefficients for the system hexane (1) + 1-chlorobutane (2): experimental (●), predicted by the Wilson model (- - -), predicted by the UNIQUAC model (—).

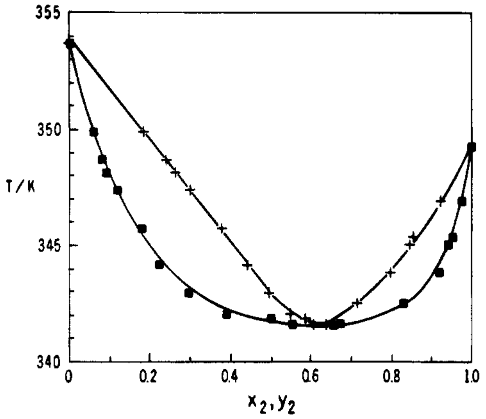

Figure 3. Boiling point diagram at 94.4 kPa for the system 1-chlorobutane (1) + 2-propanol (3).

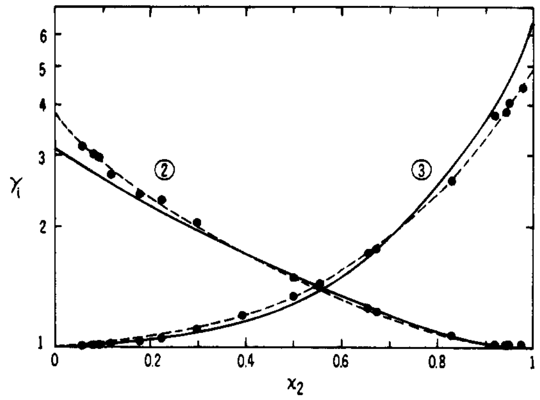

Figure 4. Activity coefficients for the system 1-chlorobutane (1) + 2-propanol (3): experimental (●), predicted by the Wilson model (- - -), predicted by the UNIFAC model (—).

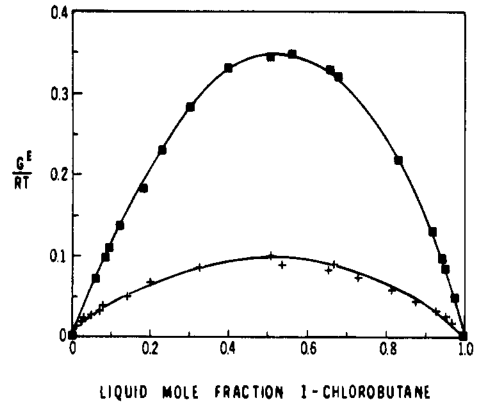

Figure 5. Variation of G^E/RT with concentration for the systems hexane + 1-chlorobutane (+) and 1-chlorobutane + 2-propanol (■) at 94.4 kPa.

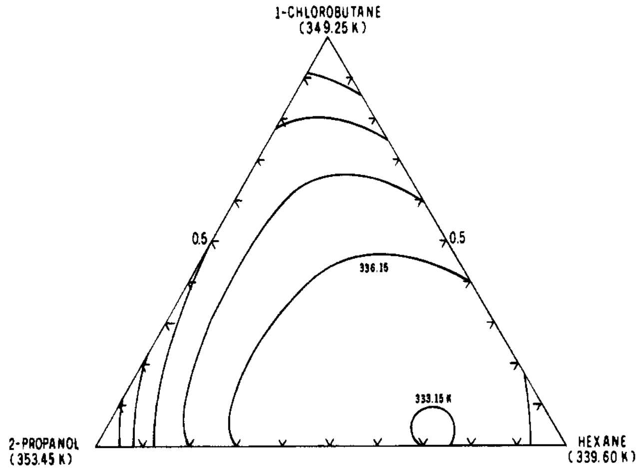

Figure 6. Isothermals for the ternary system hexane (1) + 1-chlorobutane (2) + 2-propanol (3) at 94.4 kPa from 333.35 to 348.15 K, every 3 K. The coefficients are from eq 11.

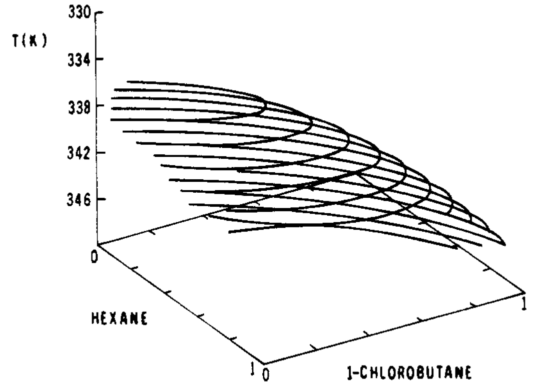

Figure 7. Three-dimensional graph of $T-x_1-x_2$.

As seen in Figures 1–4 the binary system hexane + 1-chlorobutane exhibits moderate deviations from ideality and an azeotrope that contains 97.5 mol % hexane and boils at 339.25 K. The binary system 1-chlorobutane + 2-propanol presents strong deviations from ideality and an azeotrope that contains 62.8 mol % 1-chlorobutane and boils at 341.60 K. The azeotropic conditions were determined by drawing the pertinent $y-x$ diagrams and temperature interpolation.

The binary data reported in Tables 2 and 3 were found to be thermodynamically consistent by the area test (Van Ness and Abbott, 1982) and the L–W method of Wisniak (1993). The ternary activity coefficients reported in Table 4 were found to be thermodynamically consistent as tested by the L–W method of Wisniak (1993) and the McDermot–Ellis method (1965) modified by Wisniak and Tamir (1977). In this method two experimental points, a and b, are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{4}$$

The local deviation D is given by

$$D = \sum_{i=1}^{N}(x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \tag{5}$$

where N is the number of components and the maximum

Table 4. Experimental Vapor–Liquid Equilibrium Data for Hexane (1) + 1-Chlorobutane (2) + 2-Propanol (3) at 94.4 kPa

					activity coefficients			$-B_{11}$/(cm^3·mol^{-1})	$-B_{22}$/(cm^3·mol^{-1})	$-B_{33}$/(cm^3·mol^{-1})	$-B_{12}$/(cm^3·mol^{-1})	$-B_{13}$/(cm^3·mol^{-1})	$-B_{23}$/(cm^3·mol^{-1})
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3						
332.95	0.582	0.132	0.635	0.109	1.3419	1.3972	2.1422	1416	1336	1208	1381	1335	1316
333.05	0.656	0.037	0.708	0.032	1.3252	1.4547	2.0133	1414	1335	1206	1380	1334	1315
333.05	0.691	0.060	0.693	0.050	1.2311	1.4062	2.4529	1414	1335	1206	1380	1334	1315
333.15	0.581	0.130	0.635	0.106	1.3365	1.3749	2.1194	1413	1334	1205	1379	1333	1314
333.15	0.779	0.048	0.729	0.039	1.1451	1.3656	3.1749	1413	1334	1205	1379	1333	1314
333.15	0.686	0.052	0.704	0.044	1.2566	1.4119	2.2748	1413	1334	1205	1379	1333	1314
333.15	0.590	0.046	0.688	0.040	1.4254	1.4702	1.7705	1413	1334	1205	1379	1333	1314
333.35	0.567	0.086	0.654	0.074	1.4021	1.4301	1.8417	1411	1332	1203	1377	1331	1312
333.35	0.728	0.101	0.690	0.079	1.1534	1.3166	3.1430	1411	1332	1203	1377	1331	1312
333.45	0.503	0.124	0.618	0.107	1.4877	1.4250	1.7273	1410	1331	1202	1376	1330	1311
333.45	0.588	0.104	0.646	0.087	1.3314	1.3876	2.0256	1410	1331	1202	1376	1330	1311
333.75	0.544	0.160	0.606	0.127	1.3371	1.3001	2.0819	1407	1328	1199	1373	1326	1307
333.75	0.749	0.134	0.686	0.103	1.0986	1.2557	4.1812	1407	1328	1199	1373	1326	1307
333.85	0.521	0.205	0.572	0.169	1.3128	1.3462	2.1755	1406	1327	1198	1372	1325	1306
333.85	0.524	0.164	0.595	0.133	1.3589	1.3326	1.9955	1406	1327	1198	1372	1325	1306
333.85	0.845	0.068	0.748	0.054	1.0601	1.3054	5.1876	1406	1327	1198	1372	1325	1306
333.95	0.433	0.076	0.633	0.069	1.7440	1.4763	1.3872	1405	1326	1196	1371	1324	1305
333.95	0.695	0.176	0.654	0.132	1.1210	1.2240	3.7989	1405	1326	1196	1371	1324	1305
334.05	0.422	0.189	0.560	0.157	1.5779	1.3514	1.6551	1404	1325	1195	1370	1323	1304
334.25	0.410	0.246	0.520	0.200	1.4957	1.3102	1.8424	1401	1323	1193	1368	1321	1302
334.55	0.341	0.217	0.503	0.195	1.7243	1.4379	1.5201	1398	1320	1190	1364	1317	1298
334.55	0.360	0.074	0.603	0.077	1.9603	1.6520	1.2598	1398	1320	1190	1364	1317	1298
334.65	0.383	0.312	0.474	0.253	1.4444	1.2887	1.9863	1397	1319	1189	1363	1316	1297
334.65	0.732	0.184	0.674	0.142	1.0747	1.2236	4.8754	1397	1319	1189	1363	1316	1297
334.75	0.352	0.285	0.470	0.241	1.5522	1.3453	1.7525	1396	1318	1188	1362	1315	1296
334.95	0.586	0.301	0.577	0.215	1.1371	1.1295	4.0168	1394	1317	1185	1360	1313	1294
335.15	0.300	0.307	0.439	0.262	1.6826	1.3365	1.6461	1392	1315	1183	1358	1310	1292
335.25	0.342	0.388	0.427	0.306	1.4307	1.2318	2.1282	1391	1314	1182	1357	1309	1290
335.25	0.433	0.368	0.486	0.269	1.2850	1.1395	2.6587	1391	1314	1182	1357	1309	1290
335.35	0.292	0.153	0.504	0.159	1.9750	1.6139	1.3014	1390	1313	1181	1356	1308	1289
336.05	0.244	0.269	0.412	0.256	1.8829	1.4506	1.4173	1382	1306	1174	1349	1300	1282
336.15	0.248	0.077	0.540	0.094	2.4217	1.8669	1.1225	1381	1305	1172	1348	1299	1281
336.15	0.476	0.435	0.508	0.301	1.1880	1.0485	4.4376	1381	1305	1172	1348	1299	1281
336.25	0.239	0.366	0.368	0.321	1.7109	1.3240	1.6221	1380	1304	1171	1347	1298	1279
336.75	0.203	0.219	0.401	0.238	2.1624	1.6184	1.2570	1375	1299	1166	1342	1293	1274
336.95	0.195	0.395	0.315	0.360	1.7587	1.3436	1.5837	1373	1297	1164	1340	1291	1272
336.95	0.217	0.464	0.325	0.376	1.6250	1.1963	1.8739	1373	1297	1164	1340	1291	1272
337.15	0.250	0.560	0.329	0.420	1.4233	1.1007	2.6047	1371	1295	1162	1338	1288	1270
337.15	0.309	0.561	0.377	0.400	1.3148	1.0446	3.4158	1371	1295	1162	1338	1288	1270
337.25	0.326	0.560	0.392	0.394	1.2934	1.0280	3.7022	1370	1294	1161	1337	1287	1269
337.65	0.168	0.179	0.385	0.222	2.4294	1.7911	1.1672	1366	1290	1157	1333	1283	1264
337.75	0.155	0.327	0.297	0.342	2.0311	1.5028	1.3453	1365	1289	1156	1332	1282	1263
337.95	0.142	0.434	0.250	0.412	1.8522	1.3564	1.5248	1362	1288	1153	1330	1280	1261
337.95	0.149	0.531	0.238	0.452	1.6763	1.2168	1.8540	1362	1288	1153	1330	1280	1261
338.35	0.194	0.660	0.265	0.502	1.4196	1.0706	3.0170	1358	1284	1149	1326	1275	1257
338.35	0.166	0.121	0.421	0.165	2.6356	1.9239	1.0927	1358	1284	1149	1326	1275	1257
338.45	0.125	0.470	0.219	0.441	1.8189	1.3168	1.5725	1357	1283	1148	1325	1274	1256
338.85	0.109	0.581	0.183	0.503	1.7207	1.2005	1.8638	1353	1279	1144	1321	1270	1252
339.15	0.103	0.313	0.230	0.370	2.2772	1.6228	1.2416	1350	1276	1141	1318	1267	1249
339.15	0.095	0.372	0.207	0.410	2.2044	1.5155	1.3034	1350	1276	1141	1318	1267	1249
339.25	0.110	0.661	0.175	0.538	1.6037	1.1148	2.2679	1349	1275	1140	1317	1266	1247
339.55	0.085	0.356	0.191	0.412	2.2496	1.5705	1.2672	1346	1273	1137	1314	1263	1244
339.65	0.077	0.400	0.166	0.443	2.1541	1.4950	1.3300	1345	1272	1136	1313	1262	1243
339.75	0.086	0.669	0.141	0.562	1.6311	1.1312	2.1464	1344	1271	1135	1312	1261	1242
339.85	0.061	0.544	0.116	0.530	1.8929	1.3078	1.5779	1343	1270	1134	1311	1260	1241
340.15	0.082	0.258	0.214	0.349	2.5735	1.7962	1.1526	1340	1267	1131	1308	1256	1238
340.15	0.140	0.749	0.199	0.591	1.4030	1.0488	3.2862	1340	1267	1131	1308	1256	1238
340.15	0.103	0.159	0.299	0.243	2.8489	2.0272	1.0807	1340	1267	1131	1308	1256	1238
340.15	0.052	0.567	0.101	0.546	1.9109	1.2796	1.6118	1340	1267	1131	1308	1256	1238
340.35	0.131	0.063	0.408	0.104	3.0356	2.1734	1.0461	1338	1265	1129	1307	1254	1236
341.05	0.064	0.248	0.179	0.357	2.7014	1.8586	1.1278	1331	1259	1122	1300	1247	1229
341.15	0.070	0.221	0.202	0.327	2.7611	1.9108	1.1051	1330	1258	1121	1299	1246	1228
341.85	0.099	0.826	0.149	0.673	1.4122	1.0252	3.8476	1323	1252	1114	1292	1239	1221
342.85	0.034	0.867	0.059	0.721	1.5611	1.0150	3.4569	1314	1243	1104	1283	1229	1211
343.75	0.044	0.152	0.168	0.287	3.3827	2.2406	1.0109	1305	1235	1095	1274	1220	1202
345.75	0.032	0.112	0.135	0.241	3.4864	2.3955	1.0015	1286	1217	1076	1256	1200	1182
349.65	0.012	0.044	0.073	0.128	4.4348	2.9015	0.9915	1250	1185	1040	1222	1163	1146
350.65	0.010	0.034	0.061	0.108	4.3463	3.0344	0.9786	1241	1176	1031	1213	1154	1137

Table 5. Antoine Coefficients, Eq 3 (TRC, 1974)

compound	A_i	B_i	C_i
hexane	6.000 91	1171.17	48.74
1-chlorobutane	6.051 54	1216.82	50.82
2-propanol	7.242 68	1580.92	53.54

Table 6. Constants for the Redlich−Kister Model, Eqs 7 and 9

A. Binary System (Eq 7)

system	b_{ij}	c_{ij}	d_{ij}	rmsd (γ_i)[a]	% dev[b]	max % dev[c]
hexane (1) + 1-chlorobutane (2)	0.1409	0.0004	−0.0022	0.003	1.2	4.7
hexane (1) + 2-propanol (3)[d]	0.7717	0.1283	0.1533	0.024	5.7	9.7
1-chlorobutane (2) + 2-propanol (3)	0.5937	0.0739	0.0271	0.010	2.4	3.7

B. Ternary System (Eq 9)

		rmsd (γ_i)[a]		% dev[b]		max % dev[c]	
	C_1	γ_1/γ_2	γ_1/γ_3	γ_1/γ_2	γ_1/γ_3	γ_1/γ_2	γ_1/γ_3
hexane (1)	0	0.014	0.021	8.3	8.5	17.7	26.9
+ 1-chlorobutane (2) + cyclohexane (3)	0.313 91	0.009	0.023	4.6	6.3	16.9	21.8

[a] rmsd(γ_i) = root mean square deviation, $\{\Sigma(\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}})\ 2\}^{0.5}/N$. [b] Average percent deviation. [c] Maximum percent deviation. [d] Wisniak and Akunis (1995).

Table 7. Constants for the Wilson Model (Eq 8)

A. Binary Systems

system	A_{ij}	Bi_j	rmsd(γ_i)[a] γ_i	rmsd(γ_i)[a] γ_j	% dev[b] γ_i	% dev[b] γ_j	max % dev[c] γ_i	max % dev[c] γ_j
hexane (1) + 1-chlorobutane (2)	0.880 23	0.760 66	0.005	0.011	1.6	2.6	3.8	7.5
hexane (1) + 2-propanol (3)[d]	0.466 28	0.122 41	0.028	0.023	1.9	1.8	10.4	4.4
1-chlorobutane (2) + 2-propanol (3)	0.526 81	0.304 77	0.015	0.021	2.2	1.8	5.7	5.9

B. Ternary System

	rmsd(γ_i)[a]			% dev[b]			max % dev[c]		
	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
hexane (1) + 1-chlorobutane (2) + cyclohexane (3)	0.005	0.012	0.008	1.8	3.3	1.7	6.5	16.3	6.2

[a] rmsd(γ_i) = root mean square deviation, $\{\Sigma(\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}})\ 2\}^{0.5}/N$. [b] Average percent deviation. [c] Maximum percent deviation. [d] Wisniak and Akunis (1995).

deviation $D_{\max}$ is

$$D_{\max} = \sum_{i=1}^{N}(x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + 2\sum_{i=1}^{N}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})\frac{\Delta P}{P} + \sum_{i=1}^{N}(x_{ia} + x_{ib})\{(T_a + C_i)^{-2} + (T_b + C_i)^{-2}\}\Delta T \quad (6)$$

The errors in the measurements Δx, ΔP, and ΔT were as previously indicated. The first term in eq 6 was the dominant one. For the experimental points reported here D never exceeded 0.242 while the smallest value of $D_{\max}$ was 0.383.

The excess Gibbs functions G^E of the two binary systems are presented in Tables 2 and 3 and Figure 5 as the variation of the dimensionless number (Gibbs number) 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 1-chlorobutane + 2-propanol is substantially larger than that for the binary hexane + 1-chlorobutane probably due to a larger steric influence and the association effects of the alcohol.

The activity coefficients of the two binary systems were correlated by the Redlich−Kister equation (Walas, 1985)

$$\log \gamma_i/\gamma_j = b_{ij}(x_j - x_i) + c_{ij}(6x_ix_j - 1) + d_{ij}(x_j - x_i)(1 - 8x_ix_j) \quad (7)$$

where b_{ij}, c_{ij}, and d_{ij} are the constants for the pertinent binary, and the Wilson model (Walas, 1985)

$$\ln \gamma_i = -\ln\left(\sum_{j=1}^{n} x_jA_{ij}\right) + 1 - \sum_{k=1}^{n}\left[x_kA_{ki}/\sum_{j=1}^{n} x_jA_{kj}\right] \quad (8)$$

where A_{ij}, A_{ki}, and A_{kj} are the Wilson binary parameters. The constants of the corresponding models appear in Tables 6 and 7, together with corresponding statistical parameters. A comparison between the experimental activity coefficients and those predicted by the Wilson model appears in Figures 2 and 4.

Of the local concentration models, the UNIQUAC (Abrams and Prausnitz, 1975) correlation represented the binary hexane + 1-chlorobutane well, while the UNIFAC model, as modified by Larsen et al. (1987), was appropiate for the 1-chlorobutane + 2-propanol system. Both models also predicted the azeotropic point. A comparison between the predicted activity coefficients and the experimental ones appears in Figures 2 and 4.

Table 8. Coefficients in the Correlation of Boiling Points, Eqs 10 and 11, Root Mean Square Deviations in Temperature, rmsd(*T*/K), and Percent Deviation

A. Equation 10

system	C_0	C_1	C_2	C_3	rmsd(T/K)	% dev[b]	max % dev[c]
hexane (1) + 1-chlorobutane (2)	−11.9264	1.24118	-11.9519		0.06	0.3	0.8
hexane (1) + 2-propanol (3)[d]	−43.0923	14.9947	−104.0728		0.31	2.0	4.1
1-chlorobutane (2) + 2-propanol (3)	−35.8191	9.26658	−47.0558	−31.5110	0.10	0.5	1.4

	A	B	C	rmsd(T/K)[a]	% dev[b]	max % dev[c]
hexane (1) + 1-chlorobutane (2) + cyclohexane (3)	−514.2507	571.8541		1.25	14.3	30.8

B. Equation 11

$A_{12} = -24.454$	$B_{12} = -49.697$	$C_{12} = -35.748$	rmsd(T) = 0.02
$A_{13} = 3.082$	$B_{13} = 15.799$	$C_{13} = -4.542$	% dev[b] = 0.2
$A_{23} = -21.541$	$B_{23} = -45.013$	$C_{23} = -23.583$	max % dev[c] = 1.2

[a] rmsd(T/K) = root mean square deviation, $\{\Sigma(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2\}^{0.5}/N$. [b] Average percent deviation. [c] Maximum percent deviation. [d] Wisniak and Akunis (1995).

The ternary activity coefficients were correlated very well by the Wilson model (eq 8), using the binary parameters, as shown by the statistical parameters given in Table 7.

The activity coefficients for the ternary system were also correlated by the following Redlich–Kister expansion (Hala et al., 1967):

$$\ln \gamma_1/\gamma_2 = b_{12}(x_2 - x_1) - c_{12}[(x_1 - x_2)^2 - 2x_1x_2] + d_{12}(x_2 - x_1)[(x_1 - x_2)^2 - 4x_1x_2] + x_3[b_{13} + c_{13}(2x_1 - x_3) + d_{13}(x_1 - x_3)(3x_1 - x_3) - b_{23} - c_{23}(2x_2 - x_3) - d_{23}(x_2 - x_3)(3x_2 - x_3) + C_1(x_2 - x_1)] \quad (9)$$

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 pairs of activity coefficients were obtained by cyclic rotation of the indices. Data for the binary hexane + 2-propanol have been reported elsewhere (Wisniak and Akunis, 1995). 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 6)—are statistically significant, suggesting that ternary data cannot be predicted directly from the binary systems. The differences are particularly significant in the diluted end.

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = \sum_{i=1}^{n} x_i T_i^{\circ}/\mathrm{K} + \sum_{i,j=1}^{n} \{x_i x_j \sum_{k=0}^{m} C_k(x_i - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (10)$$

In this equation n is the number of components ($n = 2$ or 3), T_i° is the boiling point of the pure component i, and m is the number of terms in the series expansion of $x_i - x_j$. C_k are the binary constants where A, B, C, and D are ternary constants. The following equation, of the same structure, can be used for the direct correlation of ternary data, without use of binary data (Tamir, 1981):

$$T/\mathrm{K} = \sum_{i=1}^{3} x_i T_i + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (11)$$

In eq 11 coefficients A_{ij}, B_{ij}, and C_{ij} are not binary constants; they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient as reflected by a lower percent average deviation and rmsd and a smaller number of parameters than those for eq 10. Both equations may require a similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 6 and 7). The various constants of eqs 10 and 11 are reported in Table 8, which also contains information indicating the degree of goodness of the correlation. It is clear that for the ternary system in question a direct fit of the data gives a much better fit.

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