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Vapor–liquid equilibria in the ternary system 1-bromopropane + 1-chlorobutane + cyclohexane

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel

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Abstract

The vapor–liquid equilibrium at 101.3 kPa has been determined for the ternary system 1-bromopropane + 1-chlorobutane + cyclohexane. The data were correlated by the Redlich–Kister 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. No ternary azeotrope is present.

Keywords: Redlich–Kister equation; Ternary system; VLE; Wisniak–Tamir equation

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List of symbols

A_i, B_i, C_i	Antoine constants, Eq. (3)
B_{ii}, B_{ij}	second molar virial coefficients, Eqs. (1) and (2)
b_{ii}, c_{ij}, d_{ii}	Redlich–Kister constants, Eq. (7)
C_k	constants, Eq. (8)
ΔG^E	excess Gibbs function
N	number of measurements
P	total pressure
P_i^0	vapor pressure of pure component 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, $[\Sigma(\gamma_{i,expt} - \gamma_{i,calc})^2]^{0.5}/N$
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

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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

1. Introduction

The present work was undertaken to measure vapor–liquid equilibria (VLE) data for the title system for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for organic halides. Data for the three binary systems have already been reported [1–3]. The binary system 1-bromopropane + 1-chlorobutane behaves ideally while the two other binaries present strong deviations from ideal behavior and an azeotropic point.

2. Experimental

2.1. Purity of materials

1-Bromopropane (99.5 mol% +) was purchased from Aldrich, 1-chlorobutane (99.5 mol% +) from Merck and cyclohexane (99.5 mol% +) from Riedel de Haen. 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.

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

Component (purity, mol%)	n_D (298.15 K)	T/K
1-Bromopropane (99.5)	1.4319 [a]	344.05 [a]
	1.4317 [b]	344.15 [b]
1-Chlorobutane (99.5)	1.3999 [a]	351.58 [a]
	1.4000 [b]	351.58 [b]
Cyclohexane (99.5)	1.4233 [a]	353.82 [a]
	1.42354 [b]	353.88 [b]

[a] Measured; [b] Ref. [13].

2.2. Apparatus and procedure

An all-glass modified Dvorak an Boublik recirculation still [4] was used in the VLE measurements. The experimental features have been described in a previous publication [5]. 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 10% SE-30. The temperatures of the column, injector and detector were 308.15, 493.15 and 543.15 K respectively. 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 units. The accuracy in determination of pressure P and temperature T was at least ± 0.1 kPa and 0.02 K, respectively.

3. Results

The temperature t, and liquid-phase x_j and vapor-phase y_j mole fraction measurements at $P = 101.3$ kPa are reported in Table 2, together with the activity coefficients γ_i which were calculated from the equation [6]

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

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 pressure P_i^0 were calculated according to the Antoine equation

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

where the constants A_i, B_i, C_i are reported in Table 3. The molar virial coefficients B_{ii}, and B_{ij} were estimated by the method of O'Connell and Prausnitz [7] 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 3% to the activity coefficient and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Table 2 and are estimated accurate to within ± 3%.

The ternary activity coefficients reported in Table 2 were found to be thermodynamically consistent as tested by the L–W method of Wisniak [8] and the McDermot–Ellis method [9] modified by Wisniak and Tamir (10). Two experimental points a and b are considered thermodynamically consistent if the following condition is fulfilled

$$D < D_{\max} \quad (4)$$

Table 2
Experimental vapor–liquid equilibria data for 1-bromopropane (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	$\mathrm{cm^3\,mol^{-1}}$					
344.40	0.836	0.051	0.844	0.043	1.0039	1.0770	1.3207	702	1227	1187	901	893	1206
344.40	0.870	0.037	0.877	0.030	1.0008	1.0124	1.3307	701	1226	1187	900	892	1206
344.60	0.788	0.065	0.803	0.054	1.0075	1.0149	1.2972	701	1225	1186	899	892	1204
344.80	0.742	0.104	0.762	0.086	1.0090	1.0187	1.2993	699	1223	1184	898	890	1203
344.80	0.794	0.080	0.809	0.065	1.0009	1.0155	1.3040	699	1223	1184	898	890	1203
344.90	0.799	0.149	0.824	0.120	1.0102	0.9918	1.4108	699	1222	1183	897	889	1202
345.00	0.726	0.085	0.749	0.070	1.0072	1.0158	1.2482	698	1221	1182	897	889	1201
345.20	0.745	0.163	0.772	0.134	1.0055	1.0044	1.3277	697	1220	1180	895	888	1199
345.20	0.647	0.142	0.680	0.120	1.0214	1.0302	1.2247	697	1220	1180	895	887	1199
345.50	0.713	0.205	0.743	0.174	1.0004	1.0191	1.3147	696	1217	1177	893	885	1196
345.70	0.712	0.213	0.747	0.176	1.0024	0.9915	1.3124	695	1215	1176	892	884	1195
345.70	0.593	0.199	0.632	0.168	1.0184	1.0119	1.2262	695	1215	1176	892	884	1195
345.90	0.632	0.261	0.668	0.225	1.0045	1.0288	1.2700	694	1214	1174	891	883	1193
345.90	0.532	0.178	0.565	0.160	1.0078	1.0658	1.2081	694	1213	1174	891	883	1193
346.30	0.474	0.158	0.525	0.139	1.0431	1.0383	1.1427	692	1211	1171	889	881	1190
346.30	0.440	0.149	0.496	0.132	1.0589	1.0416	1.1329	692	1210	1171	888	880	1190
346.60	0.578	0.355	0.616	0.313	0.9903	1.0279	1.3144	690	1207	1168	886	878	1187
346.80	0.393	0.227	0.451	0.197	1.0642	1.0077	1.1420	689	1206	1167	885	877	1186
346.80	0.427	0.278	0.482	0.241	1.0434	1.0018	1.1635	689	1206	1167	885	877	1186
346.90	0.431	0.346	0.471	0.308	1.0108	1.0269	1.2212	689	1205	1166	885	877	1185
347.10	0.356	0.120	0.422	0.113	1.0908	1.0824	1.0862	688	1204	1165	884	876	1183
347.20	0.369	0.399	0.410	0.359	1.0174	1.0275	1.2147	687	1203	1163	883	875	1182
347.30	0.320	0.350	0.364	0.319	1.0367	1.0387	1.1726	687	1202	1163	882	874	1182
347.50	0.456	0.487	0.503	0.437	0.9993	1.0155	1.2718	686	1200	1161	880	873	1179
347.60	0.329	0.094	0.384	0.094	1.0547	1.1307	1.0927	685	1200	1161	880	872	1179
347.70	0.278	0.203	0.338	0.194	1.0950	1.0777	1.0852	685	1199	1160	880	872	1178
347.70	0.429	0.528	0.485	0.467	1.0192	0.9962	1.3409	685	1199	1159	879	872	1178
347.80	0.330	0.495	0.371	0.446	1.0122	1.0120	1.2543	684	1198	1159	879	871	1178
347.80	0.250	0.276	0.301	0.263	1.0810	1.0658	1.1042	684	1198	1158	879	871	1177
348.00	0.349	0.561	0.392	0.508	1.0038	1.0106	1.3215	683	1196	1157	878	870	1176
348.30	0.362	0.594	0.408	0.541	0.9983	1.0078	1.3822	682	1194	1155	876	868	1173

348.40	0.212	0.225	0.266	0.222	1.1105	1.0902	1.0706	682	1193	1154	875	868	1173
348.40	0.227	0.482	0.263	0.451	1.0235	1.0308	1.1596	681	1193	1154	875	867	1173
348.50	0.339	0.636	0.389	0.580	1.0133	1.0040	1.3789	681	1192	1153	875	867	1172
348.50	0.240	0.080	0.318	0.084	1.1648	1.1551	1.0325	681	1192	1153	874	867	1172
348.60	0.272	0.584	0.308	0.537	0.9947	1.0067	1.2567	680	1191	1152	874	866	1171
348.60	0.273	0.567	0.312	0.522	1.0004	1.0081	1.2111	680	1191	1152	874	866	1170
348.70	0.223	0.116	0.284	0.129	1.1158	1.2160	1.0367	680	1190	1152	873	866	1170
348.70	0.299	0.657	0.347	0.603	1.0160	1.0025	1.3410	680	1190	1151	873	866	1170
348.70	0.181	0.586	0.210	0.550	1.0162	1.0238	1.1987	680	1190	1151	873	865	1170
348.90	0.161	0.533	0.190	0.505	1.0288	1.0298	1.1552	679	1189	1150	872	864	1169
348.90	0.139	0.464	0.165	0.452	1.0386	1.0591	1.1167	679	1189	1150	872	864	1169
348.90	0.176	0.188	0.234	0.194	1.1588	1.1233	1.0409	679	1188	1150	872	864	1168
348.90	0.160	0.399	0.195	0.385	1.0614	1.0471	1.1029	679	1188	1150	872	864	1168
349.00	0.196	0.638	0.228	0.595	1.0121	1.0107	1.2267	678	1188	1149	872	864	1168
349.00	0.159	0.554	0.186	0.523	1.0158	1.0212	1.1699	678	1188	1149	871	863	1167
349.00	0.259	0.665	0.297	0.623	0.9946	1.0114	1.2314	678	1187	1149	871	863	1167
349.00	0.185	0.097	0.253	0.107	1.1896	1.1913	1.0286	678	1187	1149	871	863	1167
349.10	0.219	0.662	0.253	0.618	0.9998	1.0079	1.2477	678	1187	1148	871	863	1167
349.30	0.108	0.366	0.135	0.367	1.0824	1.0762	1.0853	677	1186	1147	870	862	1165
349.40	0.232	0.742	0.271	0.698	0.9997	1.0054	1.3896	676	1184	1146	869	861	1164
349.60	0.143	0.153	0.196	0.167	1.1708	1.1571	1.0287	676	1183	1144	868	860	1163
349.70	0.072	0.375	0.093	0.383	1.1019	1.0819	1.0723	675	1182	1143	867	859	1162
349.70	0.107	0.699	0.125	0.666	0.9981	1.0097	1.2114	675	1182	1143	867	859	1162
349.80	0.168	0.784	0.199	0.747	1.0027	1.0080	1.2869	675	1182	1143	867	859	1161
349.80	0.044	0.607	0.055	0.594	1.0465	1.0336	1.1378	675	1181	1143	867	859	1161
349.80	0.138	0.110	0.195	0.125	1.2036	1.1998	1.0197	674	1181	1142	867	859	1161
349.90	0.084	0.285	0.114	0.304	1.1502	1.1235	1.0381	674	1180	1142	866	858	1160
350.10	0.079	0.257	0.108	0.277	1.1563	1.1305	1.0359	673	1179	1140	865	857	1159
350.10	0.035	0.684	0.045	0.665	1.0631	1.0160	1.1565	673	1178	1140	864	857	1158
350.20	0.141	0.048	0.206	0.060	1.2185	1.2973	1.0120	673	1178	1140	864	856	1158
350.20	0.031	0.349	0.042	0.373	1.1462	1.1148	1.0504	672	1178	1139	864	856	1158
350.40	0.098	0.078	0.153	0.095	1.2935	1.2684	1.0113	671	1176	1137	863	855	1156
350.50	0.094	0.854	0.114	0.828	1.0026	1.0020	1.2611	671	1175	1137	862	854	1155
350.60	0.102	0.874	0.122	0.847	1.0004	1.0012	1.3525	671	1175	1136	862	854	1155
351.00	0.106	0.039	0.163	0.051	1.2562	1.3489	0.9991	668	1171	1133	859	851	1151
351.80	0.068	0.052	0.110	0.068	1.2930	1.2912	0.9954	665	1165	1127	855	847	1145
352.10	0.044	0.035	0.077	0.049	1.3992	1.3985	1.0007	664	1163	1125	853	845	1143

Table 3
Antoine coefficients, Eq. (3)

Compound	A_i	B_i	C_i
1-Bromopropane[a]	6.03555	1194.889	47.64
1-Chlorobutane[a]	6.05154	1216.82	50.82
Cyclohexane[a]	5.96407	1200.31	50.65

[a] Ref. [13].

The local deviation D is given by

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

where N is the number of components and the maximum deviation $D_{\max}$ is

$$\begin{aligned} D_{\max} = & \sum_{i=1}^{N} (x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x \\ & + 2\sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N} (x_{ia} + x_{ib})\frac{\Delta P}{P} \\ & + \sum_{i=1}^{N} (x_{ia} + x_{ib})[(t_a + C_i)^{-2} + (t_b + C_i)^{-2}]\Delta t \end{aligned} \tag{6}$$

The errors in the measurements Δx, ΔP and Δt were as previously indicated. The first term in Eq. [6] is the dominant one. For the experimental points reported here, D never exceeded 0.069 while the smallest value of $D_{\max}$ was 0.374.

The activity coefficients for the ternary system were correlated by the Redlich–Kister expansion [11]

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

where b_{ij}, c_{ij} and d_{ij} are constants for the pertinent binary and C_1 is a ternary constant. The equations for the two other pairs of activity coefficients were obtained by cyclic rotation of the indices. Data for the three binary systems have been reported elsewhere [1–3]. 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 4), are statistically insignificant, suggesting that ternary data can be predicted directly from the binary systems.

Table 4
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	γ_1/γ_3
1-Bromopropane (1)	0	0	0	0.1570	−0.0077	0	0.1320	+0.0085	0.0160	0	0.005	0.004
+ 1-chlorobutane (2)												
+ cyclohexane (3)										−0.06074	0.005	0.003

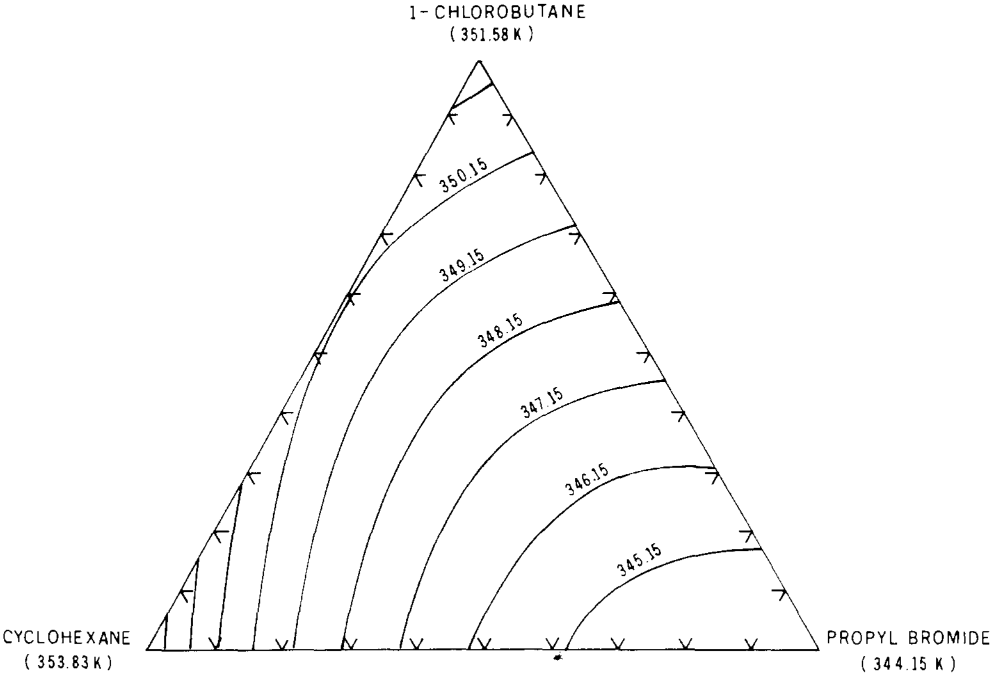

Fig. 1. Isothermals for the ternary system 1-bromopropane–1-chlorobutane–cyclohexane at 101.3 kPa. Coefficients from Eq. (8).

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir [12]

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

In these equations, n is the number of components ($n = 2$ or 3), T_i^0 is the boiling point of the pure component i (in K or °C) and l is the number of terms in the series expansion

Table 5
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	%[a]
1-Bromopropane (1) + 1-chlorobutane (2)[b]	−1.0788	−0.3199	0	0.01	0.04
1-Bromopropane (1) + cyclohexane (3)[c]	−14.163	4.8161	0	0.02	0.11
1-Chlorobutane (2) + cyclohexane (3)[d]	−10.538	1.9321	−2.1549	0.01	0.01
	A	B	C	rmsd	
1-Bromopropane (1) + 1-chlorobutane (2) + cyclohexane (3)	−2.56976	46.3007	–	0.04	

[a] Average % deviation; [b] Ref. [3]; [c] Ref. [1]; [d] Ref. [2].

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. 1). The various constants of Eq. (8) are reported in Table 5, which also contains information indicating the degree of goodness of the correlation.

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