Isothermal Vapor−Liquid Equilibrium of 1-Chlorobutane with Ethanol or 1-Hexanol at Ten Temperatures between 278.15 K and 323.15 K

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Vapor pressures of (1-chlorobutane + ethanol or 1-hexanol) at 10 temperatures between 278.15 and 323.15 K were measured by a static method. The reduction of the vapor pressures to obtain activity coefficients and excess molar Gibbs energies was carried out by fitting the vapor pressure data to the Wilson equation according to Barker's method. In the 1-chlorobutane + ethanol system, azeotropic mixtures with a minimum boiling point temperature were observed over the whole temperature range.

Introduction

Following our studies on thermodynamic properties of binary systems of alcohol + a second polar component,[1−7] we report here vapor pressures at 10 temperatures between 278.15 and 323.15 K of (1-chlorobutane + ethanol or 1-hexanol). In a previous paper[8] we reported excess molar enthalpies at 298.15 K, and excess molar volumes at 298.15 K and 308.15 K for these mixtures.

Experimental Section

Chemicals. 1-Chlorobutane was supplied by Aldrich (low water content, mole fraction > 0.995). Ethanol and 1-hexanol were Fluka products (mole fraction >0.998 and >0.990, respectively). The chemicals were stored over molecular sieves (3A) and were used without further purification. The mass fraction purity was checked by gas chromatography and found to be 0.999 for 1-chlorobutane, 0.999 for ethanol, and 0.994 for 1-hexanol.

Apparatus and Procedures. The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh,[9] except for some experimental details which are described elsewhere.[10,11] To prevent condensation effects on the mercury meniscus, the temperature of the manometer and the connecting tube containing the vapor phase was maintained at 325.0 K by circulating water thermostated to within ±0.1 K. The cell volume was about 12 cm^3, and 8 to 10 cm^3 were used in each experiment. Each liquid was degassed by magnetic stirring under its own vapor pressure before mixing. They were added successively, by gravity, into the cell immersed in liquid nitrogen. The masses of both components were determined by weighing. Uncertainties in the mole fractions are estimated to be less than 0.0003. Manometric readings were performed with a cathetometer to within ±0.01 mm, and pressure reproducibility was estimated to be 10 Pa. The temperature of the liquid was controlled to within ±10 mK.

Results

The molar volumes of the pure components used in the Barker analysis together with the experimental vapor pressures, which are compared with values calculated from equations found in the literature, are presented in Table 1. Experimental vapor pressures of 1-chlorobutane at 10 temperatures between 278.15 and 323.15 K (Table 1) were fitted with an Antoine equation

$$\ln(P/\text{kPa}) = 13.594\,839 - \frac{2631.025}{(T/\text{K}) - 58.734} \qquad (1)$$

Vapor pressures obtained from eq 1 show a standard deviation of 20 Pa and a maximum deviation of −39 Pa at $T = 298.15$ K.

The second virial coefficient, at $T = 325.0$ K, of 1-chlorobutane ($B_{11} = -1340$ cm^3·mol^{-1}) was taken from the TRC tables,[17] that of ethanol ($B_{22} = -2625$ cm^3·mol^{-1}) was obtained by extrapolation from the Dymond and Smith[18] data compilation, and that of 1-hexanol ($B_{22} = -7850$ cm^3·mol^{-1}) was calculated from the Tsonopoulos[19] correlation. The mixed virial coefficient was calculated according to a cubic combination rule

$$B_{12} = \frac{1}{8}(B_{11}^{1/3} + B_{22}^{1/3})^3 \qquad (2)$$

Table 2 shows our vapor pressure measurements along with the activity coefficients γ_1 and γ_2, and the excess molar Gibbs free energy G^E values fitted by Barker's method[20] to the Wilson[21] correlation. The activity coefficients are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (3)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (4)$$

with

$$\Lambda_{ij} = \frac{V_j^\circ}{V_i^\circ}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \qquad (5)$$

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Table 1. Molar Volumes V° and Vapor Pressures P° of the Pure Compounds Used in the Barker Analysis

	1-chlorobutane			ethanol			1-hexanol		
		P°/kPa			P°/kPa			P°/kPa	
T/K	$V^{\circ\,a}$/(cm^3·mol^{-1})	b	c	$V^{\circ\,d}$/(cm^3·mol^{-1})	b	e	$V^{\circ\,d}$/(cm^3·mol^{-1})	b	f
278.15	102.7	4.981	5.000	57.4	2.237	2.249	123.1	0.016	0.017
283.15	103.3	6.513	6.519	57.7	3.142	3.135	123.6	0.027	0.029
288.15	103.9	8.381	8.405	58.2	4.310	4.313	124.1	0.048	0.047
293.15	104.5	10.694	10.723	58.4	5.856	5.861	124.6	0.072	0.072
298.15	105.2	13.499	13.547	58.7	7.871	7.874	125.2	0.105	0.109
303.15	105.8	16.971	16.956	59.0	10.475	10.462	125.7	0.163	0.164
308.15	106.5	21.050	21.038	59.3	13.776	13.755	126.3	0.248	0.241
313.15	107.2	25.878	25.890	59.7	17.956	17.904	126.9	0.367	0.349
318.15	107.9	31.589	31.615	60.0	23.067	23.084	127.5	0.520	0.497
323.15	108.6	38.258	38.324	60.3	29.379	29.494	128.1	0.723	0.700

[a] TRC.[12] [b] This work. [c] TRC.[13] [d] TRC.[14] [e] Ambrose and Ghiassee.[15] [f] TRC.[16]

Table 2. Values of the Vapor Pressure P, Deviations $\Delta P = P - P_{calc}$, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Energies G^E

x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})	x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})
					1-Chlorobutane (1) + Ethanol (2)						
					278.15 K						
0.0697	6.041	8	1.0354	7.8828	407	0.4984	6.062	−2	1.7620	1.4837	1112
0.0960	6.083	−14	1.0584	6.1739	523	0.5977	5.922	2	2.0925	1.2873	1036
0.1038	6.115	5	1.0658	5.7984	554	0.6275	5.877	20	2.2132	1.2424	999
0.1312	6.129	−11	1.0937	4.7703	654	0.7020	5.641	5	2.5752	1.1510	880
0.1325	6.115	−26	1.0951	4.7293	659	0.7197	5.601	35	2.6763	1.1332	846
0.2160	6.173	2	1.1969	3.0825	888	0.8078	5.074	−6	3.2965	1.0625	643
0.2739	6.171	1	1.2820	2.4923	995	0.8115	5.050	−3	3.3281	1.0601	634
0.4069	6.133	0	1.5315	1.7586	1116	0.9187	3.876	−29	4.5022	1.0116	307
					283.15 K						
0.0696	7.925	−12	1.0331	7.6177	404	0.4985	8.033	−1	1.7468	1.4783	1117
0.0957	8.047	9	1.0550	6.0316	519	0.5979	7.850	−1	2.0723	1.2838	1041
0.1035	8.061	2	1.0621	5.6732	550	0.6277	7.790	21	2.1910	1.2395	1005
0.1311	8.087	−20	1.0893	4.6878	652	0.7023	7.495	12	2.5468	1.1489	885
0.1324	8.077	−33	1.0907	4.6479	656	0.7199	7.449	54	2.6454	1.1314	851
0.2159	8.179	18	1.1903	3.0519	889	0.8080	6.763	−6	3.2520	1.0615	647
0.2739	8.165	−1	1.2738	2.4736	998	0.8118	6.711	−22	3.2833	1.0591	637
0.4070	8.126	5	1.5198	1.7502	1121	0.9188	5.232	−31	4.4235	1.0114	309
					288.15 K						
0.0695	10.279	0	1.0311	7.4106	402	0.4986	10.468	−17	1.7345	1.4770	1127
0.0953	10.438	7	1.0519	5.9308	516	0.5982	10.240	−17	2.0574	1.2830	1052
0.1032	10.474	11	1.0589	5.5845	548	0.6279	10.174	18	2.1751	1.2387	1015
0.1309	10.534	−6	1.0854	4.6312	651	0.7027	9.815	19	2.5286	1.1484	894
0.1323	10.504	−38	1.0868	4.5919	656	0.7202	9.707	22	2.6255	1.1310	859
0.2159	10.632	4	1.1843	3.0352	892	0.8083	8.897	0	3.2272	1.0613	653
0.2738	10.642	1	1.2665	2.4653	1003	0.8121	8.855	5	3.2588	1.0589	643
0.4071	10.600	9	1.5097	1.7475	1129	0.9189	6.961	−31	4.3875	1.0113	312
					293.15 K						
0.0693	13.232	23	1.0297	7.2207	400	0.4985	13.567	−8	1.7226	1.4727	1135
0.0947	13.438	11	1.0493	5.8360	513	0.5985	13.280	−10	2.0426	1.2797	1059
0.1032	13.499	22	1.0567	5.4760	548	0.6283	13.187	24	2.1588	1.2358	1021
0.1306	13.564	−27	1.0823	4.5686	651	0.7032	12.716	6	2.5078	1.1463	899
0.1323	13.539	−58	1.0839	4.5229	657	0.7205	12.600	28	2.6022	1.1292	865
0.2159	13.748	16	1.1796	3.0087	895	0.8087	11.571	−8	3.1933	1.0603	657
0.2737	13.731	−24	1.2606	2.4497	1008	0.8126	11.527	7	3.2250	1.0579	646
0.4069	13.708	4	1.5006	1.7408	1136	0.9192	9.171	−20	4.3253	1.0111	313
					298.15 K						
0.0694	16.805	15	1.0281	7.0038	399	0.4989	17.383	−25	1.7109	1.4696	1143
0.0949	17.128	23	1.0472	5.6989	513	0.5982	17.063	−3	2.0249	1.2790	1068
0.1027	17.193	21	1.0536	5.3875	545	0.6279	16.937	27	2.1393	1.2354	1030
0.1308	17.327	−20	1.0791	4.4960	651	0.7039	16.365	19	2.4894	1.1449	905
0.1321	17.291	−63	1.0803	4.4622	656	0.7202	16.211	24	2.5770	1.1290	873
0.2157	17.555	−11	1.1740	2.9879	897	0.8092	14.937	−10	3.1664	1.0598	662
0.2736	17.601	−6	1.2536	2.4381	1011	0.8122	14.917	26	3.1903	1.0579	653
0.4070	17.564	4	1.4907	1.7363	1144	0.9194	11.950	−41	4.2819	1.0110	315
					303.15 K						
0.0692	21.216	75	1.0258	6.7082	392	0.4989	22.108	−46	1.6917	1.4662	1145
0.0940	21.617	33	1.0432	5.5450	502	0.5986	21.713	−26	2.0016	1.2765	1070
0.1019	21.712	26	1.0494	5.2506	535	0.6284	21.561	12	2.1143	1.2332	1033
0.1304	21.906	−46	1.0740	4.4009	643	0.7031	20.892	17	2.4515	1.1449	911
0.1317	21.896	−66	1.0752	4.3686	648	0.7206	20.681	18	2.5445	1.1278	876
0.2155	22.276	−19	1.1658	2.9552	892	0.8086	19.196	31	3.1150	1.0598	667
0.2734	22.341	−26	1.2433	2.4205	1008	0.8128	19.085	17	3.1481	1.0571	655
0.4072	22.322	−10	1.4760	1.7295	1144	0.9198	15.489	−16	4.2159	1.0108	316

Table 2. (Continued)

x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})	x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})
308.15 K											
0.0689	26.443	118	1.0241	6.4697	386	0.4991	27.831	−46	1.6762	1.4597	1146
0.0926	26.972	54	1.0399	5.4278	493	0.5992	27.344	−34	1.9816	1.2720	1072
0.1007	27.123	56	1.0460	5.1424	526	0.6290	27.090	−58	2.0922	1.2293	1034
0.1298	27.340	−121	1.0700	4.3163	637	0.7040	26.331	8	2.4240	1.1420	911
0.1311	27.427	−48	1.0712	4.2848	642	0.7213	26.109	39	2.5136	1.1254	877
0.2152	27.936	−36	1.1595	2.9201	888	0.8092	24.265	22	3.0706	1.0585	666
0.2730	28.048	−43	1.2351	2.3997	1005	0.8137	24.163	45	3.1045	1.0558	654
0.4075	28.080	−2	1.4646	1.7184	1144	0.9193	19.885	24	4.1248	1.0108	318
313.15 K											
0.0684	32.623	104	1.0226	6.2659	381	0.4994	34.733	−87	1.6624	1.4523	1148
0.0906	33.364	81	1.0367	5.3447	481	0.6000	34.180	−45	1.9637	1.2668	1072
0.0989	33.576	75	1.0426	5.0614	515	0.6299	33.955	7	2.0726	1.2247	1035
0.1288	33.992	−86	1.0664	4.2440	631	0.7052	32.971	25	2.3994	1.1386	910
0.1302	34.033	−65	1.0676	4.2122	636	0.7222	32.679	34	2.4851	1.1226	876
0.2147	34.765	−60	1.1538	2.8867	885	0.8101	30.453	22	3.0287	1.0569	665
0.2723	34.929	−81	1.2275	2.3802	1003	0.8149	30.320	49	3.0640	1.0541	651
0.4074	35.017	−33	1.4535	1.7081	1145	0.9198	25.199	28	4.0453	1.0104	317
318.15 K											
0.0677	39.786	19	1.0207	6.0548	373	0.4995	43.012	−126	1.6463	1.4498	1151
0.0877	40.875	161	1.0326	5.2779	463	0.6011	42.383	−60	1.9464	1.2641	1075
0.0983	41.249	144	1.0397	4.9344	508	0.6311	42.149	33	2.0544	1.2223	1038
0.1274	41.819	−70	1.0618	4.1830	621	0.7070	40.902	−13	2.3804	1.1364	911
0.1289	41.857	−64	1.0630	4.1503	626	0.7234	40.618	50	2.4627	1.1212	878
0.2145	42.894	−92	1.1473	2.8575	881	0.8114	37.954	38	3.0012	1.0560	665
0.2711	43.154	−110	1.2178	2.3715	999	0.8166	37.776	68	3.0390	1.0530	651
0.4074	43.332	−53	1.4409	1.7031	1146	0.9204	31.683	45	4.0011	1.0102	317
323.15 K											
0.0673	48.669	327	1.0195	5.8727	368	0.5000	52.869	−184	1.6338	1.4424	1151
0.0836	49.569	180	1.0287	5.2624	442	0.6017	52.177	−69	1.9287	1.2595	1076
0.0952	50.116	133	1.0360	4.8956	492	0.6328	51.816	−28	2.0386	1.2170	1037
0.1253	50.980	−131	1.0578	4.1368	610	0.7094	50.387	−4	2.3627	1.1320	908
0.1312	51.080	−200	1.0625	4.0134	631	0.7251	50.021	29	2.4397	1.1178	876
0.2135	52.525	−144	1.1417	2.8299	877	0.8132	46.917	112	2.9679	1.0540	661
0.2692	52.862	−208	1.2094	2.3600	994	0.8189	46.657	127	3.0085	1.0508	645
0.4073	53.202	−114	1.4306	1.6932	1146	0.9214	39.534	167	3.9323	1.0098	313
1-Chlorobutane (1) + 1-Hexanol (2)											
278.15 K											
0.1036	4.721	11	1.0537	3.7583	426	0.6008	3.486	6	1.7461	1.1398	696
0.1977	4.590	18	1.1424	2.3520	638	0.7036	2.932	18	1.9673	1.0692	573
0.3044	4.390	−8	1.2674	1.7169	762	0.7760	2.374	−28	2.1450	1.0371	461
0.3843	4.233	5	1.3765	1.4659	795	0.8645	1.633	9	2.3898	1.0128	298
0.4790	3.936	−26	1.5238	1.2812	782	0.9018	1.252	16	2.5036	1.0065	222
283.15 K											
0.1037	6.175	26	1.0519	3.7256	428	0.6011	4.540	2	1.7411	1.1407	707
0.1978	5.981	19	1.1391	2.3490	644	0.7038	3.810	9	1.9631	1.0697	582
0.3046	5.736	4	1.2629	1.7186	770	0.7762	3.121	−16	2.1417	1.0375	468
0.3845	5.497	−13	1.3714	1.4678	805	0.8646	2.140	15	2.3885	1.0129	304
0.4792	5.138	−25	1.5184	1.2828	793	0.9020	1.631	12	2.5034	1.0066	226
288.15 K											
0.1038	7.947	34	1.0514	3.6620	430	0.6015	5.790	−10	1.7290	1.1366	707
0.1980	7.669	1	1.1379	2.3180	647	0.7041	4.866	19	1.9442	1.0676	582
0.3047	7.350	−15	1.2603	1.7017	773	0.7764	3.966	−28	2.1160	1.0362	468
0.3847	7.105	33	1.3672	1.4563	807	0.8648	2.717	17	2.3524	1.0124	303
0.4794	6.583	−34	1.5114	1.2755	795	0.9021	2.076	19	2.4619	1.0064	225
293.15 K											
0.1039	10.110	43	1.0480	3.5610	424	0.6020	7.326	6	1.7111	1.1356	708
0.1982	9.753	24	1.1313	2.2909	641	0.7046	6.143	30	1.9227	1.0671	582
0.3049	9.334	9	1.2504	1.6928	770	0.7767	5.000	−38	2.0915	1.0360	469
0.3850	8.915	−30	1.3552	1.4518	805	0.8650	3.416	11	2.3243	1.0123	303
0.4797	8.331	−31	1.4967	1.2733	794	0.9023	2.622	26	2.4319	1.0063	226
298.15 K											
0.1038	12.772	78	1.0465	3.4844	422	0.6026	9.145	−7	1.6963	1.1320	706
0.1980	12.272	22	1.1278	2.2616	640	0.7051	7.635	9	1.9018	1.0653	580
0.3052	11.735	13	1.2452	1.6769	769	0.7771	6.245	−30	2.0647	1.0350	467
0.3854	11.206	−25	1.3481	1.4414	804	0.8653	4.248	14	2.2888	1.0120	302
0.4802	10.442	−40	1.4868	1.2669	793	0.9025	3.285	57	2.3919	1.0061	225
303.15 K											
0.1039	15.967	55	1.0431	3.3669	413	0.6035	11.334	−20	1.6756	1.1303	702
0.1983	15.356	47	1.1207	2.2267	630	0.7059	9.459	6	1.8764	1.0645	578
0.3051	14.621	5	1.2337	1.6664	761	0.7776	7.745	−34	2.0355	1.0347	465
0.3851	13.960	−26	1.3336	1.4365	798	0.8657	5.281	30	2.2546	1.0118	301
0.4807	13.003	−26	1.4700	1.2634	788	0.9027	4.062	52	2.3553	1.0061	224

Table 2. (Continued)

x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})	x_2	P/kPa	ΔP/Pa	γ_1	γ_2	G^E/(J·mol^{-1})
					308.15 K						
0.1041	19.752	53	1.0407	3.2550	406	0.6032	13.894	−33	1.6527	1.1278	697
0.1987	18.944	36	1.1155	2.1851	622	0.7068	11.556	9	1.8494	1.0626	572
0.3055	18.037	26	1.2251	1.6482	752	0.7782	9.453	−43	2.0022	1.0337	461
0.3857	17.176	−30	1.3222	1.4253	790	0.8661	6.439	33	2.2127	1.0115	298
0.4802	15.993	−21	1.4533	1.2584	781	0.9030	4.965	65	2.3089	1.0059	221
					313.15 K						
0.1044	24.158	−25	1.0389	3.1611	402	0.6043	16.925	−6	1.6359	1.1245	692
0.1992	23.218	52	1.1115	2.1483	617	0.7065	14.046	−8	1.8243	1.0616	569
0.3061	22.068	44	1.2182	1.6317	747	0.7789	11.472	−39	1.9747	1.0328	457
0.3864	20.994	−13	1.3132	1.4150	784	0.8667	7.791	25	2.1777	1.0112	295
0.4809	19.474	−47	1.4411	1.2525	776	0.9034	6.020	69	2.2701	1.0057	220
					318.15 K						
0.1048	29.535	60	1.0371	3.0666	397	0.6058	20.384	−33	1.6197	1.1211	686
0.1999	28.226	51	1.1076	2.1106	611	0.7077	16.900	−16	1.8024	1.0599	564
0.3068	26.758	29	1.2114	1.6148	741	0.7799	13.820	−24	1.9479	1.0319	453
0.3874	25.439	−16	1.3042	1.4045	778	0.8674	9.363	25	2.1437	1.0108	292
0.4819	23.569	−45	1.4289	1.2464	770	0.9039	7.265	95	2.2325	1.0056	217
					323.15 K						
0.1053	35.725	77	1.0357	2.9748	393	0.6079	24.375	−34	1.6045	1.1171	679
0.2009	34.052	46	1.1043	2.0710	606	0.7093	20.162	−20	1.7812	1.0579	558
0.3079	32.252	59	1.2054	1.5963	734	0.7791	16.589	−27	1.9170	1.0315	451
0.3887	30.592	−14	1.2962	1.3926	772	0.8682	11.166	37	2.1094	1.0105	289
0.4833	28.259	−78	1.4177	1.2393	763	0.9045	8.673	110	2.1941	1.0054	215

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 3, 4, and 10

	1-chlorobutane (1) + ethanol (2)			1-chlorobutane (1) + 1-hexanol (2)		
T/K	Λ_{12}	Λ_{21}	σ/Pa	Λ_{12}	Λ_{21}	σ/Pa
278.15	0.4262	0.0729	15	0.8701	0.0966	17
283.15	0.4320	0.0817	22	0.8634	0.1031	17
288.15	0.4322	0.0902	17	0.8809	0.1042	25
293.15	0.4373	0.0970	23	0.8810	0.1168	29
298.15	0.4389	0.1056	26	0.8940	0.1222	39
303.15	0.4412	0.1189	37	0.8952	0.1373	36
308.15	0.4476	0.1293	59	0.9056	0.1487	40
313.15	0.4552	0.1386	64	0.9147	0.1583	40
318.15	0.4555	0.1514	86	0.9228	0.1689	48
323.15	0.4628	0.1605	161	0.9328	0.1785	61

Table 4. Azeotropic Pressures and Mole Fractions for the System {(1 − z) 1-Chlorobutane + z Ethanol}

T/K	z(exptl)	P_z(exptl)/kPa	z(calcd from eq 11)	P_z(calcd from eq 13)/kPa
278.15	0.245	6.172	0.244	6.213
283.15	0.259	8.166	0.259	8.167
288.15	0.274	10.640	0.274	10.633
293.15	0.288	13.756	0.289	13.720
298.15	0.304	17.612	0.304	17.553
303.15	0.318	22.383	0.319	22.274
308.15	0.334	28.128	0.334	28.047
313.15	0.349	35.086	0.349	35.058
318.15	0.364	43.410	0.364	43.516
323.15	0.379	53.328	0.379	53.654

where the subscripts 1 and 2 stand for 1-chlorobutane and alcohol, respectively. $V°$ is the molar volume and λ's are the interaction constants between the molecules designated in the subscripts. The vapor pressure is then given by

$$P_{\text{calc}} = x_1\gamma_1P_1^\circ R_1 + x_2\gamma_2P_2^\circ R_2 \tag{6}$$

where the nonideality of the vapor phase is accounted for with the corrections

$$R_1 = \exp\{[(V_1^\circ - B_{11})(P - P_1^\circ) - P\delta_{12}y_2^2]/RT\} \tag{7}$$

$$R_2 = \exp\{[(V_2^\circ - B_{22})(P - P_2^\circ) - P\delta_{12}y_1^2]/RT\} \tag{8}$$

where y_1 and y_2 are the vapor phase mole fractions of 1-chlorobutane and alcohol, respectively, and δ_{12}

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{9}$$

For a given composition, the sample temperature is changed and a slight variation of the true liquid mole fraction may be detected in Table 2, according to the variable composition of the vapor phase. In Table 3, the Wilson parameters Λ_{12} and Λ_{21} are collected, together with the standard deviations defined by

$$\sigma(P) = \{\sum_{i=1}^{N}(\Delta P)_i^2/(N - 2)\}^{1/2} \tag{10}$$

ΔP's are the residual pressures according to Barker's method, and N is the number of experimental points. Vapor pressure−liquid composition curves are shown in Figure 1. For both systems, Figure 2 shows the analytic equations for G^E at the lowest and highest temperatures. A negative temperature coefficient can be observed for the mixtures (1-chlorobutane + 1−hexanol).

We test the consistency of the enthalpies and free energies by means of the Gibbs−Helmholtz equation. The coefficients $\partial\Lambda_{ij}/\partial T$ have been obtained by fitting the Wilson parameters as a linear function of the temperature. The H^E values, calculated at $T = 298.15$ K, are shown as curves in Figure 3 together with the H^E experimental data found in the literature. The agreement is reasonable considering that the quantitative evaluation of H^E from vapor pressures involves considerable uncertainty.[23] In the same figure and at the same temperature, TS^E curves, obtained from $TS^E = H^E - G^E$, are also plotted.

For (1-chlorobutane + ethanol), azeotropic mixtures with a minimum boiling temperature were observed over the whole range of temperature. Azeotropic mole fractions z were graphically calculated, assuming ideal behavior of the vapor, from the well-known equation, $\gamma_1/\gamma_2 = P_2^\circ/P_1^\circ$. Azeotropic compositions show a linear relation with the temperature according to the equation

$$z = a + b(T/\text{K}) \tag{11}$$

with $a = -0.5874$ and $b = 2.990 \times 10^{-3}$ K^{-1}.

Table 5. Thermodynamic Excess Functions for 0.5 Alkanol + 0.5 1-Chlorobutane or + 0.5 *n*-Hexane, at 298.15 K

	ethanol			1-hexanol		
solvent	H^E/(J·mol^{-1})	TS^E/(J·mol^{-1})	V^E/(cm^3·mol^{-1})	H^E/(J·mol^{-1})	TS^E/(J·mol^{-1})	V^E/(cm^3·mol^{-1})
1-chlorobutane	706[a]	−437[b]	0.136[a]	905[a]	121[b]	0.030[a]
n-hexane[c]	555	−850	0.41	465	−515	−0.16

[a] Pérez et al.[8] [b] This work. [c] Brown et al.[24]

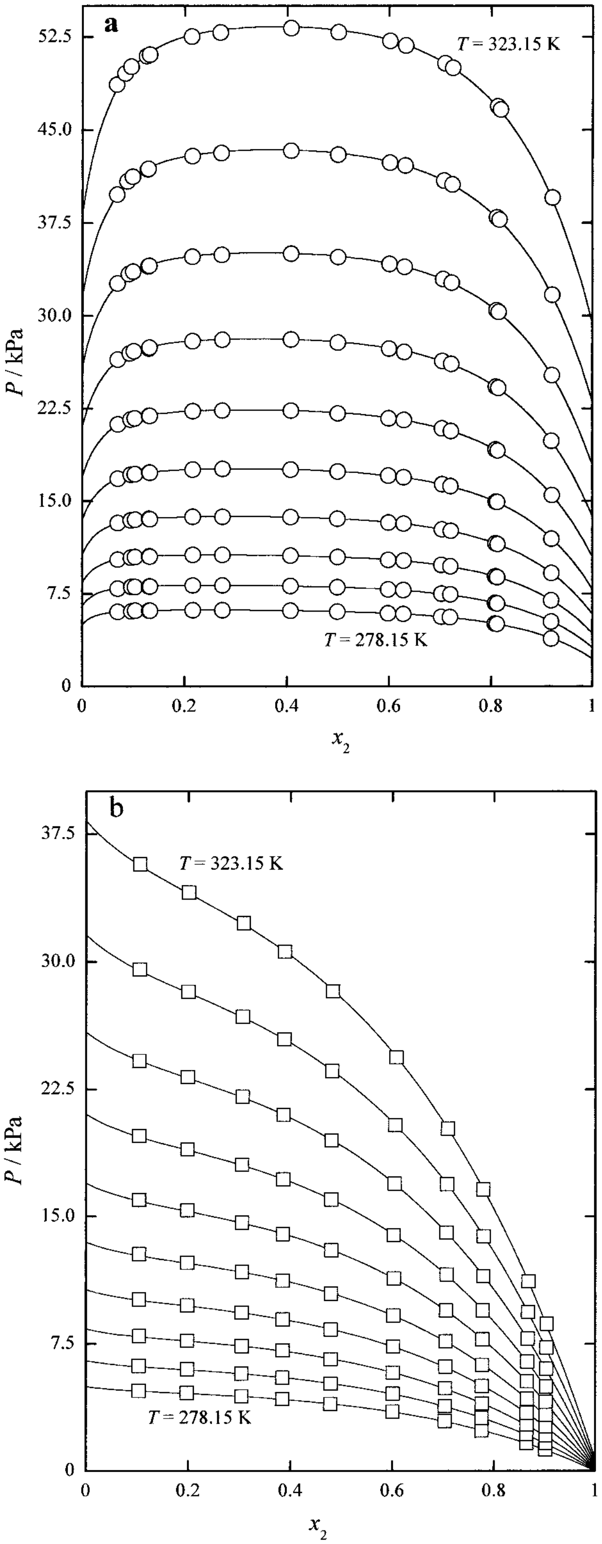

Figure 1. Vapor pressures at 5-deg intervals of temperature from 278.15 to 323.15 K: (a) {x_1 1-chlorobutane + x_2 ethanol}; (b) {x_1 1-chlorobutane + x_2 1-hexanol}, plotted against liquid-phase composition of alcohol.

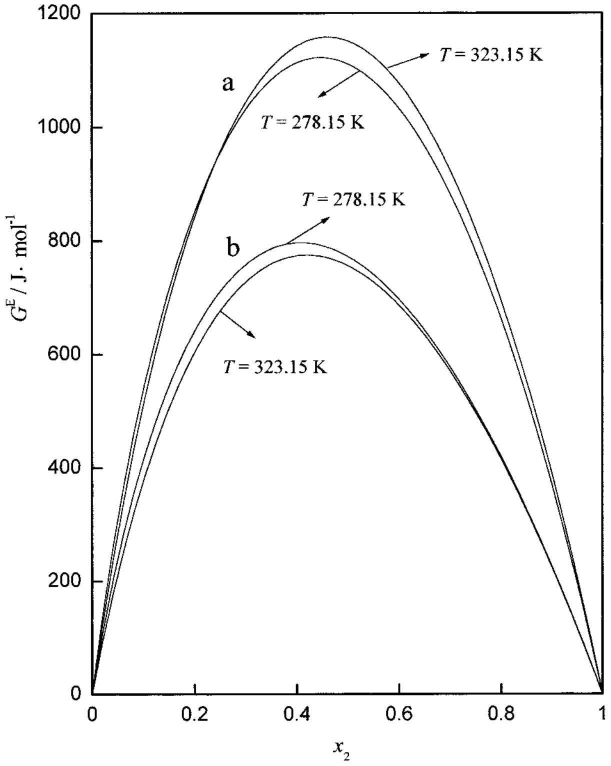

Figure 2. Excess molar Gibbs energies G^E at 278.15 K and 323.15 K: (a) {x_1 1-chlorobutane + x_2 ethanol}; (b) {x_1 1-chlorobutane + x_2 1-hexanol}, plotted as a function of mole fraction of alcohol.

Along the azeotropic line, assuming both ideal behavior of the vapor phase and negligible volume of the liquid phase, the Clausius−Clapeyron equation

$$\mathrm{d}\ln P_z/\mathrm{d}T = \Delta_{\mathrm{vap}}H_z/RT^2 \qquad (12)$$

is satisfied. If we accept that the enthalpy of azeotropic vaporization is constant, the azeotropic pressure is related with the temperature in a similar way to that shown by a pure substance

$$\ln(P_z/\mathrm{Pa}) = A + B(T/\mathrm{K})^{-1} \qquad (13)$$

with $A = 24.22$ and $B = -4306$ K. Experimental and calculated (from eqs 11 and 13) azeotropic compositions and pressures are compared in Table 4.

In Table 5, thermodynamic excess functions of ethanol or 1-hexanol with 1-chlorobutane and *n*-hexane as inert solvent, at $x = 0.5$ and 298.15 K, are briefly summarized.

In mixtures of ethanol or 1-hexanol with 1-chlorobutane as a polar solvent ($\mu = 2.1$ D, from McClelland[25]), solvent−solvent and hydroxyl-group−solvent interactions come into play and the excess molar enthalpies and entropies are much more positive than those for *n*-hexane in place of 1-chlorobutane. Both these increases are consistent if more hydrogen bonds are broken at a given mole fraction due to the interaction between the hydroxyl hydrogen and the chlorine atom. On the other hand, the excess enthalpy and

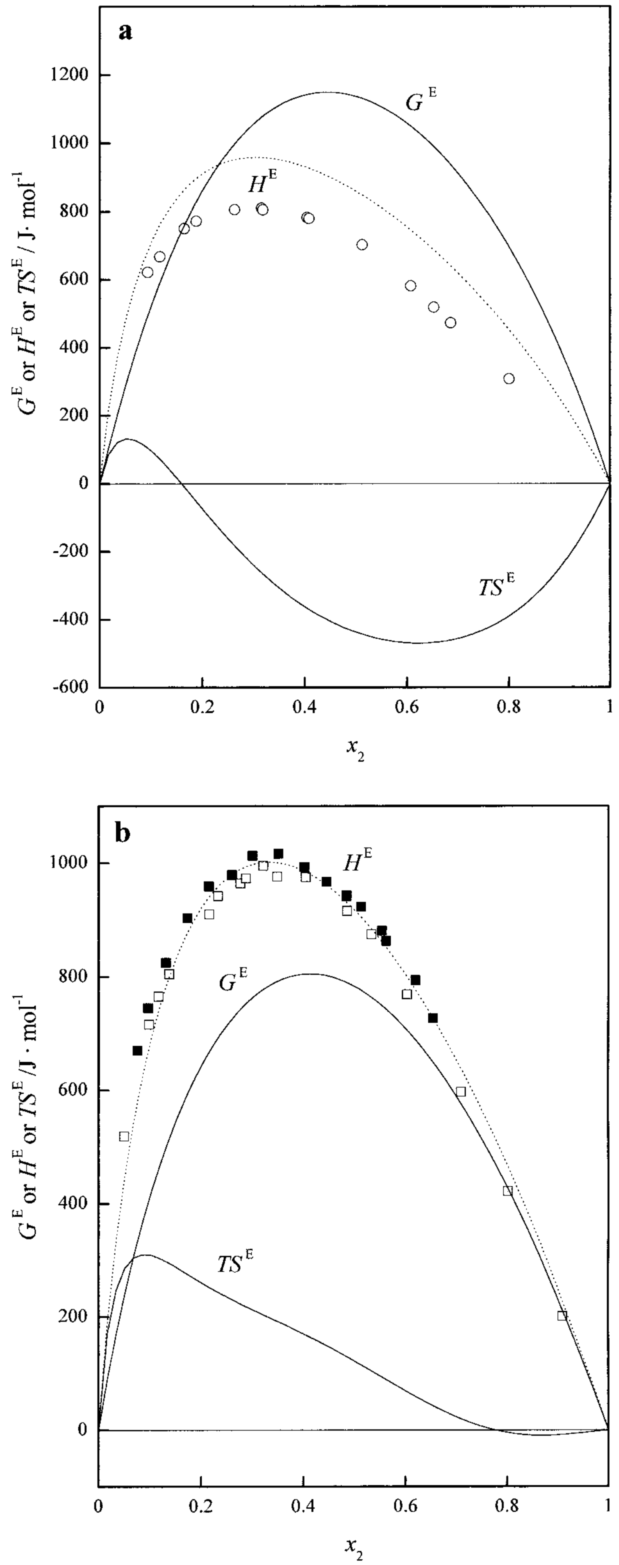

Figure 3. Thermal excess molar functions, at $T = 298.15$ K. (a) $\{x_1$ 1-chlorobutane + x_2 ethanol$\}$: (○) experimental H^E (Pérez et al.[8]). (b) $\{x_1$ 1-chlorobutane + x_2 1-hexanol$\}$: (□) experimental H^E (Pérez et al.[8]); (■) (Santana et al.[22]). (···) Gibbs−Helmholtz H^E; (—) G^E and TS^E.

excess entropy become more positive on going from ethanol to 1-hexanol, as is observed in Figure 3. Presumably, the strong entropy increase in mixtures with specific interactions is associated with a large gain in configurational freedom on breaking hydrogen bonds.

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