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Isothermal Vapor−Liquid Equilibrium of Butanone + Butan-1-ol at Eight Temperatures between 278.15 and 323.15 K

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Vapor pressures of butanone + butan-1-ol, at eight temperatures between 278.15 and 323.15 K, were measured by a static method. Activity coefficients and excess molar Gibbs free energies G^E were calculated by Barker's method. Reduction of the vapor pressure data is carried out by means of the Redlich−Kister and Wilson correlations.

Introduction

In the last few years, much experimental work has been devoted to mixtures of alcohol + alkane but not so much to mixtures of alcohol + a second polar component whose molecules may compete with alcohol molecules for hydrogen-bond formation. This type of thermodynamic information is necessary for a better understanding of the hydrogen bonding and for the development and testing of models and theories of associated systems in the liquid state. In a previous paper (Iñarrea *et al.*, 1988) excess enthalpies and volumes of butanone + butan-1-ol were measured at 298.15 and 308.15 K. In this paper we report vapor pressures at eight temperatures between 278.15 and 323.15 K. Isothermal vapor pressure measurements on this mixture have not been found in the literature.

Experimental Section

Butanone (better than 99.5 mol % pure) and butan-1-ol (better than 99.5 mol % pure) were Fluka products. The liquids were kept over activated molecular sieves (0.3 nm) and used witout further purification.

The total vapor pressure measurements were performed by a static method. Some experimental details are described elsewhere (Pardo *et al.*, 1987; Gracia *et al.*, 1992). For preventing condensation effects on the mercury meniscus, the temperature of the manometer was maintained at 325.0 K by circulating water thermostated to ±0.1 K. Manometer readings were made with a Wild KM-305 cathetometer to ±0.01 mm, and the pressure reproducibility was estimated to be better than 15 Pa. The temperature of the liquid sample was maintained constant within 10 mK, and the uncertainty in the mole fraction was less than 0.0003.

Results

Molar volumes and vapor pressures of the pure compounds are collected in Table 1. The second virial coefficients, at 325.0 K, of butanone ($B_{11} = -1840$ cm^3 mol^{-1}) and butan-1-ol ($B_{22} = -1890$ cm^3 mol^{-1}) were calculated from the values listed by Dymond and Smith (1969). We assume that the vapor is an ideal mixture of imperfect gases:

$$B_{12} = \frac{(B_{11} + B_{22})}{2} \tag{1}$$

Table 1. Vapor Pressure *P* and Molar Volumes *V* of the Pure Compounds in the Barker Analysis

	butanone			butan-1-ol		
		P^0/kPa			P^0/kPa	
T/K	V^0/cm^3·mol^{-1} [a]	this work	lit.[b]	V^0/cm^3·mol^{-1} [c]	this work	lit.[d]
278.15	87.88	4.277	4.278	90.32	0.196	0.189
288.15	88.99	7.334	7.342	90.90	0.452	0.427
293.15	89.56	9.435	9.459	91.45	0.655	0.625
298.15	90.14	12.071	12.060	92.02	0.944	0.901
303.15	90.72	15.281	15.231	92.59	1.328	1.280
308.15	91.32	19.110	19.060	93.17	1.855	1.793
313.15	91.93	23.683	23.649	93.74	2.532	2.477
323.15	93.19	35.540	35.548	94.95	4.610	4.556

[a] TRC (1991). [b] Ambrose (1975). [c] Gracia (1992). [d] Ambrose (1987).

Table 2 shows our vapor pressure measurements along with the vapor phase composition, the activity coefficients γ_1 and γ_2, and the excess molar Gibbs free energy G^E values fitted to the Redlich-Kister and Wilson (Wilson, 1964) correlations. The activity coefficients are given by

Redlich−Kister:

$$\ln \gamma_1 = x^2[A_0 + \sum_{f=1}^{m}\{A_f(1 - 2x)^f + 2fA_f(1 - x)(1 - 2x)^{f-1}\}] \tag{2}$$

$$\ln \gamma_2 = (1 - x)^2[A_0 + \sum_{f=1}^{m}\{A_f(1 - 2x)^f - 2fA_fx(1 - 2x)^{f-1}\}] \tag{3}$$

where x stands for the mole fraction of butan-1-ol in the liquid phase.

Wilson:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{4}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{5}$$

x_2 being the mole fraction of butan-1-ol.

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Table 2. Experimental Vapor Pressure Data, Vapor Phase Composition, Activity Coefficients, and Excess Molar Gibbs Energy Calculated from Redlich−Kister and Wilson Correlations for C_4H_8O (1) + C_4H_9OH (2)

		Redlich−Kister				Wilson						Redlich−Kister				Wilson			
x_2	P/kPa	y_2	γ_1	γ_2	G^E/J·mol^{-1}	y_2	γ_1	γ_2	G^E/J·mol^{-1}	x_2	P/kPa	y_2	γ_1	γ_2	G^E/J·mol^{-1}	y_2	γ_1	γ_2	G^E/J·mol^{-1}
		278.15 K										303.15 K							
0.0633	4.068	0.0078	1.0058	2.5271	148	0.0075	1.0046	2.4392	140	0.0634	14.605	0.0119	1.0040	2.0309	123	0.0117	1.0034	1.9966	118
0.1813	3.733	0.0186	1.0428	1.9412	358	0.0186	1.0364	1.9475	347	0.1815	13.319	0.0310	1.0303	1.6833	300	0.0311	1.0272	1.6870	295
0.3451	3.282	0.0312	1.1404	1.5059	526	0.0315	1.1313	1.5223	522	0.3459	11.632	0.0556	1.1037	1.3868	448	0.0559	1.0996	1.3941	446
0.4282	3.086	0.0374	1.2104	1.3698	564	0.0376	1.2051	1.3770	564	0.4291	10.788	0.0689	1.1579	1.2856	483	0.0690	1.1558	1.2884	482
0.5270	2.780	0.0466	1.3168	1.2492	572	0.0465	1.3207	1.2457	572	0.5278	9.755	0.0868	1.2405	1.1925	491	0.0866	1.2430	1.1902	491
0.6886	2.238	0.0673	1.5772	1.1125	498	0.0667	1.5975	1.1019	492	0.6895	7.799	0.1286	1.4374	1.0851	426	0.1279	1.4472	1.0794	422
0.7396	2.045	0.0768	1.6953	1.0809	451	0.0761	1.7156	1.0708	442	0.7403	7.062	0.1489	1.5223	1.0606	385	0.1482	1.5316	1.0553	379
0.8391	1.573	0.1082	2.0105	1.0331	323	0.1076	2.0064	1.0271	311	0.8396	5.374	0.2138	1.7367	1.0242	274	0.2131	1.7338	1.0211	267
0.9159	1.017	0.1784	2.3720	1.0097	188	0.1780	2.3038	1.0075	178	0.9162	3.705	0.3318	1.9639	1.0069	159	0.3315	1.9325	1.0058	153
0.9655	0.577	0.3285	2.6910	1.0017	83	0.3284	2.5416	1.0013	77	0.9656	2.408	0.5341	2.1510	1.0012	69	0.5339	2.0857	1.0010	66
		288.15 K										308.15 K							
0.0634	6.994	0.0095	1.0048	2.2877	136	0.0092	1.0040	2.2347	131	0.0634	18.249	0.0132	1.0041	1.9969	122	0.0129	1.0034	1.9582	117
0.1814	6.390	0.0237	1.0362	1.8291	332	0.0237	1.0319	1.8336	325	0.1816	16.675	0.0340	1.0311	1.6477	297	0.0341	1.0274	1.6519	290
0.3453	5.596	0.0410	1.1224	1.4596	494	0.0413	1.1165	1.4702	492	0.3456	14.609	0.0608	1.1033	1.3607	438	0.0612	1.0987	1.3687	436
0.4284	5.234	0.0499	1.1858	1.3377	532	0.0500	1.1825	1.3422	532	0.4288	13.584	0.0753	1.1553	1.2650	470	0.0755	1.1531	1.2678	469
0.5271	4.718	0.0624	1.2830	1.2273	541	0.0623	1.2858	1.2248	541	0.5275	12.260	0.0955	1.2329	1.1783	475	0.0952	1.2362	1.1751	475
0.6888	3.809	0.0905	1.5193	1.1011	471	0.0899	1.5326	1.0938	466	0.6899	9.737	0.1434	1.4148	1.0788	410	0.1425	1.4264	1.0717	405
0.7398	3.446	0.1045	1.6241	1.0721	426	0.1038	1.6371	1.0653	419	0.7407	8.781	0.1669	1.4921	1.0562	370	0.1659	1.5030	1.0496	363
0.8392	2.634	0.1487	1.8954	1.0290	304	0.1481	1.8923	1.0250	295	0.8394	6.722	0.2386	1.6854	1.0227	263	0.2376	1.6814	1.0188	254
0.9160	1.759	0.2379	2.1942	1.0084	176	0.2375	2.1506	1.0069	169	0.9163	4.732	0.3630	1.8919	1.0065	152	0.3625	1.8536	1.0051	144
0.9655	1.035	0.4228	2.4480	1.0015	77	0.4227	2.3546	1.0012	74	0.9656	3.120	0.5758	2.0611	1.0011	67	0.5756	1.9827	1.0009	63
		293.15 K										313.15 K							
0.0634	8.995	0.0103	1.0047	2.2118	134	0.0101	1.0038	2.1514	127	0.0635	22.627	0.0141	1.0039	1.9254	118	0.0138	1.0032	1.8892	113
0.1815	8.233	0.0260	1.0354	1.7779	324	0.0260	1.0303	1.7835	315	0.1817	20.680	0.0367	1.0291	1.6079	286	0.0368	1.0256	1.6122	280
0.3455	7.203	0.0454	1.1175	1.4328	480	0.0458	1.1106	1.4451	477	0.3458	18.099	0.0664	1.0971	1.3426	423	0.0668	1.0926	1.3505	421
0.4285	6.714	0.0557	1.1769	1.3198	517	0.0559	1.1732	1.3248	516	0.4290	16.808	0.0827	1.1459	1.2530	454	0.0828	1.1439	1.2558	454
0.5273	6.033	0.0702	1.2677	1.2169	526	0.0700	1.2712	1.2137	525	0.5277	15.145	0.1052	1.2192	1.1711	461	0.1049	1.2225	1.1680	460
0.6890	4.872	0.1023	1.4882	1.0980	458	0.1015	1.5038	1.0893	453	0.6904	12.058	0.1582	1.3918	1.0760	398	0.1571	1.4032	1.0691	393
0.7399	4.396	0.1186	1.5864	1.0703	415	0.1177	1.6016	1.0622	407	0.7411	10.876	0.1841	1.4651	1.0543	359	0.1830	1.4757	1.0479	353
0.8393	3.358	0.1690	1.8430	1.0286	297	0.1682	1.8392	1.0238	287	0.8401	8.361	0.2622	1.6493	1.0219	256	0.2612	1.6455	1.0181	247
0.9161	2.270	0.2670	2.1289	1.0083	173	0.2665	2.0778	1.0065	164	0.9164	5.952	0.3943	1.8436	1.0063	148	0.3938	1.8074	1.0049	141
0.9656	1.389	0.4562	2.3739	1.0015	76	0.4560	2.2650	1.0011	71	0.9657	4.061	0.6041	2.0037	1.0011	65	0.6039	1.9297	1.0008	61
		298. 15 K										323.15 K							
0.0634	11.494	0.0110	1.0038	2.0781	124	0.0109	1.0034	2.0520	121	0.0635	34.021	0.0162	1.0032	1.8101	109	0.0161	1.0029	1.7974	107
0.1816	10.499	0.0286	1.0299	1.7266	306	0.0286	1.0276	1.7294	302	0.1820	31.127	0.0434	1.0248	1.5522	269	0.0435	1.0235	1.5539	267
0.3457	9.159	0.0511	1.1051	1.4168	461	0.0513	1.1020	1.4224	459	0.3461	27.278	0.0795	1.0866	1.3171	402	0.0797	1.0850	1.3201	402
0.4288	8.522	0.0629	1.1621	1.3083	498	0.0630	1.1605	1.3106	498	0.4294	25.281	0.0994	1.1328	1.2333	433	0.0995	1.1321	1.2343	433
0.5275	7.709	0.0788	1.2507	1.2075	509	0.0787	1.2524	1.2060	509	0.5281	22.798	0.1266	1.2026	1.1556	439	0.1265	1.2040	1.1543	439
0.6892	6.181	0.1157	1.4653	1.0909	443	0.1153	1.4722	1.0870	441	0.6899	18.264	0.1894	1.3625	1.0666	377	0.1889	1.3669	1.0639	375
0.7401	5.637	0.1329	1.5584	1.0644	400	0.1324	1.5651	1.0608	397	0.7407	16.749	0.2171	1.4282	1.0468	339	0.2166	1.4323	1.0443	337
0.8395	4.269	0.1913	1.7934	1.0255	285	0.1909	1.7916	1.0233	280	0.8400	12.847	0.3106	1.5859	0.1082	239	0.3101	1.5845	1.0167	235
0.9161	2.918	0.2994	2.0412	1.0072	165	0.2991	2.0192	1.0065	161	0.9168	9.270	0.4613	1.7426	1.0051	137	0.4611	1.7289	1.0045	134
0.9656	1.831	0.4992	2.2449	1.0013	72	0.4992	2.1988	1.0011	70	0.9658	6.679	0.6692	1.8634	1.0009	59	0.6691	1.8358	1.0008	58

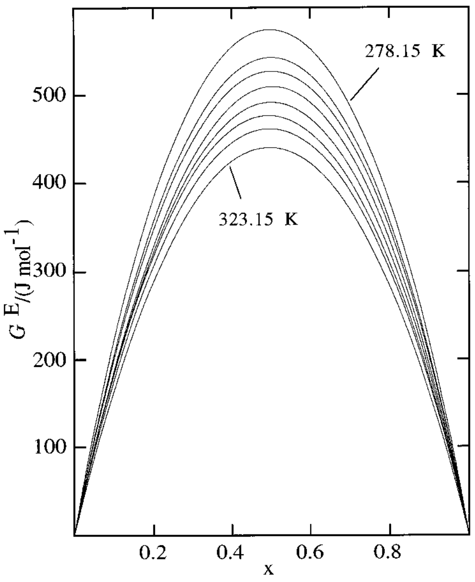

Figure 1. Excess molar Gibbs energies G^E, between 278.15 and 323.15 K, for $(1 - x)C_4H_8O + xC_4H_9OH$.

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 2 and 5 for C_4H_8O (1) + C_4H_9OH (2)

	Redlich–Kister				Wilson		
T/K	A_0	A_1	A_2	$\sigma(P)$/Pa	Λ_{12}	Λ_{21}	$\sigma(P)$/Pa
278.15	0.9928	0.0095	0.1047	13	0.5775	0.5434	23
288.15	0.9056	−0.0017	0.0722	17	0.5965	0.5931	26
293.15	0.8646	−0.0040	0.0801	20	0.6110	0.6114	36
298.15	0.8222	−0.0155	0.0430	18	0.6041	0.6529	25
303.15	0.7809	−0.0021	0.0524	29	0.6478	0.6428	41
308.15	0.7448	0.0152	0.0596	23	0.7028	0.6189	50
313.15	0.7103	0.0081	0.0568	27	0.7040	0.6458	59
323.15	0.6561	0.0090	0.0256	73	0.7247	0.6706	75

The vapor pressure is then given by

$$P_{\text{calc}} = x_1\gamma_1P_1^0R_1 + x_2\gamma_2P_2^0R_2 \qquad (6)$$

using for nonideality of the vapor phase the corrections

$$R_1 = \exp\{[(V_1^0 - B_{11})(P - P_1^0) - P\delta_{12}y_2^{\,2}]/RT\} \qquad (7)$$

$$R_2 = \exp\{[(V_2^0 - B_{22})(P - P_2^0) - P\delta_{12}y_1^{\,2}]/RT\} \qquad (8)$$

y_1 and y_2 are the vapor phase mole fractions of butanone and butan-1-ol, respectively, and δ_{12}

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \qquad (9)$$

in our case taken equal to zero. Redlich–Kister and Wilson parameters were determined by Barker's method (Barker, 1953).

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 coefficients of eqs 2–5 together with the standard deviations defined by

$$\sigma(P) = [\sum_{i=1}^{N}(\delta P)_i^{\,2}/(N - m)]^{1/2} \qquad (10)$$

are collected. δP's are the residual pressures according to Barker's method; N is the number of experimental points, and m is the number of parameters in the corresponding analytical equation. Apparently, and according to the standard deviations, the vapor pressure data are better represented by the Redlich–Kister correlation. We have tested other biparametric correlation models (Van Laar, NRTL, and UNIQUAC), observing a similar behavior to the Wilson equation. Excess molar Gibbs energy curves are shown in Figure 1, and a negative temperature coefficient is observed. This system has been measured (Aristovich *et al.*, 1965) at 323.15 K. From these experimental results we have calculated $G^E(x{=}0.5) = 403$ J·mol^{-1}, which is about 10% lower than our experimental value.

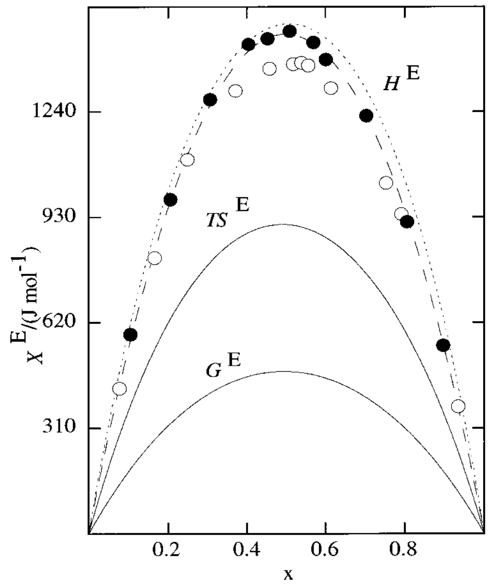

Figure 2. Thermodynamic excess functions, at 308.15 K, for $(1 - x)C_4H_8O + xC_4H_9OH$: (○) H^E-experimental values (Iñarrea *et al.*, 1988); (●) H^E-experimental values (Nagata *et al.*, taken from Christensen *et al.*, 1984); (···) from the Gibbs–Helmholtz equation and Redlich–Kister correlation; (- - -) from Gibbs–Helmholtz and Wilson equations.

In the absence of independent values of the activity coefficients we cannot use the Gibbs–Duhem relation to test the thermodynamic consistency of the vapor pressure measurements. We can, however, test the consistency of the enthalpies and free energies by means of the Gibbs–Helmholtz equation. By assuming that A_i and Λ_{ij} vary linearly with the temperature, the H^E-calculated values are shown as curves in Figure 2 together with H^E-experimental data, at 308.15 K. Apparently, the Wilson correlation gives a somewhat better consistency than that of the Redlich–Kister one. In the same figure and at the same temperature TS^E and G^E curves are also plotted.

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