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Excess Gibbs Free Energies at Several Temperatures of Butanone with 1-Hexanol or 1-Octanol

Rosa Garriga, Francisco Sánchez, Pascual Pérez, and Mariano Gracia*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza,
50009 Zaragoza, Spain

Vapor pressures of butanone + 1-hexanol or 1-octanol, at several temperatures between 288.15 K 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

Following our thermodynamic study of binary mixtures of alcohol + a second polar component (Garriga *et al.*, 1996a−d), we report here vapor pressures at several temperatures between 288.15 K and 323.15 K of (butanone + 1-hexanol or 1-octanol). In a previous paper (Iñarrea *et al.*, 1988) excess enthalpies and volumes were measured at 298.15 K and 308.15 K. Isothermal vapor pressure measurements on these mixtures have not been found in the literature.

Experimental Section

Butanone, 1-hexanol, and 1-octanol were Fluka products (purity greater than 99.5 mol %). All the liquids were kept over activated molecular sieves (3A) and used without further purification.

The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh (1968). The experimental details are described elsewhere (Pardo *et al.*, 1987; Gracia *et al.*, 1992). To prevent 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. Most of the vapor phase was also maintained at 325.0 K. Each liquid was degassed by magnetic stirring under its own vapor pressure before mixing. Manometric readings were performed with a cathetometer to ±0.01 mm, and pressure reproducibility was estimated to be better than 15 Pa. The temperature of the liquid sample was controlled to ±10 mK. Uncertainties in the mole fractions are estimated to be less than 0.0003.

Results

Table 1 shows the molar volumes of the pure compounds used in the Barker analysis together with the experimental vapor pressures, which are compared with values calculated from equations found in the literature. The second virial coefficient, at 325.0 K, of butanone ($B_{11} = -1840$ cm^3 mol^{-1}) was obtained from the Dymond and Smith (1980) compilation, and those of 1-hexanol ($B_{22} = -7850$ cm^3 mol^{-1}) and 1-octanol ($B_{22} = -19\,850$ cm^3 mol^{-1}) were calculated from the Tsonopoulos (1974) correlation. We assume that the vapor phase is an ideal mixture of imperfect gases:

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

Vapor pressures of the pure compounds, at ten temperatures for butanone and 1-hexanol and at seven temperatures for 1-octanol (see Table 1), were fitted to Antoine equations:

Butanone:

$$\ln(p/\mathrm{kPa}) = 14.133009 - \frac{2843.871}{T/\mathrm{K} - 53.875} \qquad (2)$$

1-Hexanol:

$$\ln(p/\mathrm{kPa}) = 8.472727 - \frac{1275.055}{T/\mathrm{K} - 178.568} \qquad (3)$$

1-Octanol:

$$\ln(p/\mathrm{kPa}) = 13.058110 - \frac{2443.493}{T/\mathrm{K} - 162.071} \qquad (4)$$

Vapor pressures obtained from eq 2 show a standard deviation of 25 Pa and a maximum deviation of −39 Pa at 323.15 K. For 1-hexanol and 1-octanol, the standard deviations are 3 Pa and the maxima +6 Pa and −5 Pa, both at 323.15 K, respectively.

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 (1964) correlations. The activity coefficients are given by

Redlich−Kister:

$$\ln \gamma_1 = x^2 \left[A_0 + \sum_{f=1}^{m}\{A_f(1 - 2x)^f + 2fA_f(1 - x)(1 - 2x)^{f-1}\}\right] \qquad (5)$$

$$\ln \gamma_2 = (1 - x)^2 \left[A_0 + \sum_{f=1}^{m}\{A_f(1 - 2x)^f - 2fA_f x(1 - 2x)^{f-1}\}\right] \qquad (6)$$

where x stands for the mole fraction of alcohol in the liquid phase.

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Table 1. Vapor Pressure P0 and Molar Volumes V0 of the Pure Compounds Used in the Barker Analysis

	butanone			hexan-1-ol			octan-1-ol		
	V^0/	P^0/Pa		V^0/	P^0/Pa		V^0/	P^0/Pa	
T/K	$cm^3 \cdot mol^{-1}$ [a]	this work	lit.[b]	$cm^3 \cdot mol^{-1}$ [c]	this work	lit.[d]	$cm^3 \cdot mol^{-1}$ [c]	this work	lit.[e]
278.15	87.88	4277	4278		13	17		<2	<1
283.15		5644	5638		24	29		<2	<2
288.15	88.99	7334	7342	124.12	45	47		<2	3
293.15	89.56	9435	9459	124.64	68	72	157.70	3	5
298.15	90.14	12071	12060	125.19	113	109	158.37	8	9
303.15	90.72	15281	15231	125.73	169	164	159.05	15	15
308.15	91.32	19110	19060	126.29	251	241	159.74	25	25
313.15	91.93	23683	23649	126.87	369	349	160.44	45	40
318.15		29132	29106		517	497		77	63
323.15	93.19	35540	35548	128.06	713	700	161.90	116	95

[a] TRC (1991). [b] Ambrose (1975). [c] TRC (1966). [d] TRC (1965). [e] TRC (1968).

Wilson:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (7)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (8)$$

x_2 being the mole fraction of alcohol.

The vapor pressure is then given by

$$P_{calc} = x_1\gamma_1P_1^0R_1 + x_2\gamma_2P_2^0R_2(9) \qquad (9)$$

using for nonideality of the vapor phase the corrections

$$R_1 = \exp\{[(V_1^0 - B_{11})(P - P_1^0) - P\delta_{12}y_2^2]/RT\} \qquad (10)$$

$$R_2 = \exp\{[(V_2^0 - B_{22})(P - P_2^0) - P\delta_{12}{y_1}^2]/RT\} \qquad (11)$$

y_1 and y_2 are the vapor phase mole fractions of butanone and alcohol, respectively, and δ_{12}

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

in our case taken equal to zero. Redlich–Kister and Wilson parameters were determined by Barker's method (Barker, 1953). Vapor pressures are plotted in Figure 1.

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 5–8 together with the standard deviations defined by

$$\sigma(P) = [\sum_{i=1}^{N}(\delta P)_i^{\,2}/(N - m)]^{1/2} \qquad (13)$$

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. Redlich–Kister and Wilson correlations give somewhat different values for the excess Gibbs free energies. For both systems, G^E curves are shown in Figure 2 and a negative temperature coefficient can be observed.

We test the consistency of the enthlapies 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 according to the Wilson correlation are shown as curves in Figure 3 together with

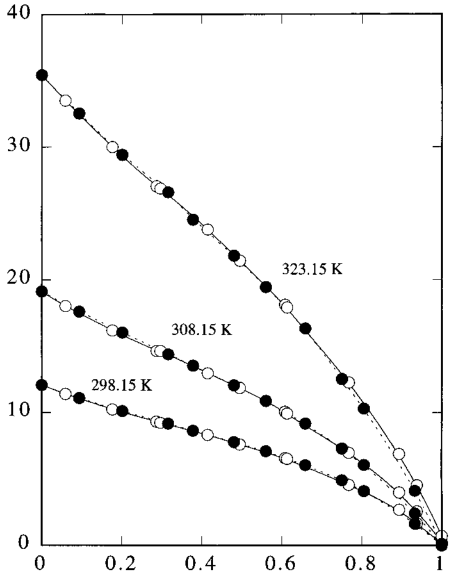

Figure 1. Vapor pressures for $(1 - x)C_4H_8O + xC_6H_{13}OH$ [(○) experimental, (—) Wilson equation] and for $(1 - x)C_4H_8O + xC_8H_{17}OH$ [(●) experimental, (···) Wilson equation].

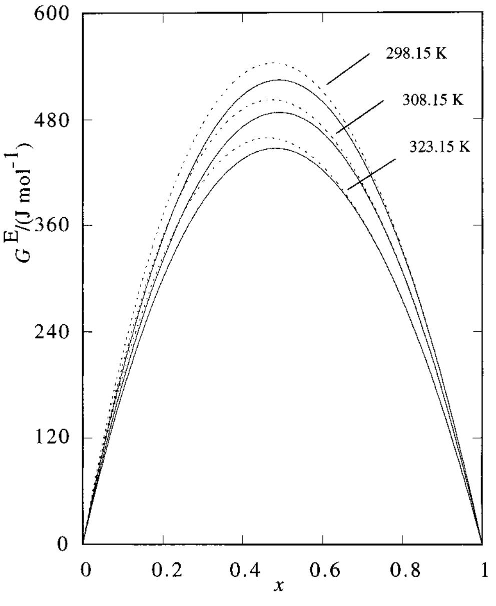

Figure 2. Excess molar Gibbs energies G^E for (—) $(1 - x)C_4H_8O + xC_6H_{13}OH$ and for (···) $(1 - x)C_4H_8O + xC_8H_{17}OH$.

Table 2. Experimental Vapor Pressure Data, Vapor Phase Composition, Activity Coefficients, and Excess Molar Gibbs Energy Calculated from Redlich−Kister and Wilson Correlations

		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}
Butanone (1) + Hexan-1-ol (2)									
T = 288.15 K									
0.0000	7.327	0.0000	1.0000	2.8466	0	0.0000	1.0000	2.6910	0
0.0592	6.889	0.0010	1.0048	2.4262	137	0.0009	1.0040	2.3583	131
0.1767	6.285	0.0024	1.0388	1.8838	343	0.0024	1.0342	1.8868	335
0.2854	5.710	0.0036	1.0944	1.5818	468	0.0037	1.0875	1.5954	463
0.2956	5.685	0.0037	1.1007	1.5597	477	0.0038	1.0938	1.5730	472
0.4133	5.140	0.0050	1.1878	1.3570	544	0.0050	1.1837	1.3619	543
0.4937	4.713	0.0061	1.2642	1.2587	557	0.0060	1.2655	1.2564	556
0.6075	4.116	0.0078	1.4046	1.1550	529	0.0078	1.4160	1.1462	526
0.6126	4.022	0.0080	1.4121	1.1511	527	0.0080	1.4238	1.1422	523
0.7661	2.872	0.0129	1.7041	1.0582	403	0.0128	1.7167	1.0498	392
0.8926	1.745	0.0236	2.1081	1.0133	220	0.0235	2.0679	1.0104	209
0.9372	1.093	0.0392	2.3113	1.0047	137	0.0391	2.2249	1.0036	128
1.0000	0.045	1.0000	2.6804	1.0000	0	1.0000	2.4842	1.0000	0
T = 293.15 K									
0.0000	9.438	0.0000	1.0000	2.6452	0	0.0000	1.0000	2.5827	0
0.0592	8.925	0.0011	1.0042	2.3053	130	0.0011	1.0038	2.2766	128
0.1767	8.010	0.0028	1.0347	1.8379	331	0.0028	1.0327	1.8385	327
0.2856	7.335	0.0042	1.0869	1.5589	454	0.0042	1.0839	1.5645	452
0.2958	7.283	0.0043	1.0930	1.5380	463	0.0043	1.0899	1.5435	461
0.4136	6.570	0.0058	1.1779	1.3417	530	0.0059	1.1760	1.3438	530
0.4941	5.996	0.0071	1.2537	1.2446	542	0.0071	1.2541	1.2436	542
0.6079	5.236	0.0092	1.3920	1.1428	514	0.0091	1.3970	1.1389	512
0.6129	5.138	0.0094	1.3991	1.1391	511	0.0093	1.4043	1.1351	510
0.7664	3.654	0.0151	1.6739	1.0510	386	0.0151	1.6795	1.0472	381
0.8927	2.157	0.0286	2.0224	1.0112	208	0.0286	2.0044	1.0099	203
0.9374	1.333	0.0482	2.1871	1.0039	128	0.0481	2.1488	1.0034	124
1.0000	0.068	1.0000	2.4697	1.0000	0	1.0000	2.3841	1.0000	0
T = 298.15 K									
0.0000	12.058	0.0000	1.0000	2.4996	0	0.0000	1.0000	2.4519	0
0.0592	11.400	0.0013	1.0038	2.2023	125	0.0013	1.0036	2.1803	123
0.1768	10.246	0.0036	1.0323	1.7837	318	0.0036	1.0307	1.7842	315
0.2859	9.326	0.0054	1.0814	1.5273	439	0.0055	1.0790	1.5316	437
0.2959	9.229	0.0056	1.0870	1.5083	447	0.0056	1.0846	1.5125	445
0.4140	8.326	0.0076	1.1675	1.3241	513	0.0076	1.1660	1.3256	512
0.4945	7.586	0.0093	1.2394	1.2323	525	0.0093	1.2398	1.2314	525
0.6083	6.569	0.0121	1.3705	1.1354	498	0.0121	1.3745	1.1322	496
0.6132	6.503	0.0123	1.3771	1.1320	495	0.0123	1.3812	1.1287	494
0.7668	4.553	0.0202	1.6353	1.0481	374	0.0202	1.6395	1.0450	369
0.8929	2.693	0.0382	1.9559	1.0105	201	0.0382	1.9416	1.0094	197
0.9375	1.664	0.0644	2.1049	1.0036	124	0.0643	2.0749	1.0032	121
1.0000	0.113	1.0000	2.3575	1.0000	0	1.0000	2.2913	1.0000	0
T = 303.15 K									
0.0000	15.309	0.0000	1.0000	2.3103	0	0.0000	1.0000	2.2805	0
0.0593	14.456	0.0015	1.0033	2.0728	117	0.0015	1.0031	2.0592	115
0.1770	12.931	0.0041	1.0283	1.7232	301	0.0041	1.0272	1.7238	299
0.2863	11.730	0.0064	1.0726	1.4976	417	0.0064	1.0710	1.5005	416
0.2963	11.606	0.0066	1.0777	1.4804	426	0.0066	1.0761	1.4833	425
0.4145	10.470	0.0090	1.1521	1.3112	492	0.0090	1.1512	1.3124	492
0.4951	9.493	0.0111	1.2198	1.2245	506	0.0111	1.2200	1.2241	505
0.6089	8.173	0.0146	1.3445	1.1315	481	0.0146	1.3470	1.1296	481
0.6136	8.069	0.0148	1.3506	1.1283	479	0.0148	1.3531	1.1263	479
0.7673	5.666	0.0243	1.5978	1.0465	363	0.0243	1.6004	1.0447	360
0.8931	3.322	0.0464	1.9018	1.0101	196	0.0463	1.8936	1.0094	193
0.9378	2.085	0.0768	2.0422	1.0035	120	0.0768	2.0249	1.0032	118
1.0000	0.169	1.0000	2.2761	1.0000	0	1.0000	2.2383	1.0000	0
T = 308.15 K									
0.0000	19.141	0.0000	1.0000	2.2977	0	0.0000	1.0000	2.2312	0
0.0593	18.035	0.0018	1.0036	2.0415	117	0.0017	1.0032	2.0116	114
0.1769	16.207	0.0048	1.0296	1.6823	297	0.0048	1.0272	1.6834	293
0.2868	14.644	0.0074	1.0741	1.4611	409	0.0075	1.0707	1.4670	406
0.2966	14.647	0.0076	1.0790	1.4451	417	0.0076	1.0756	1.4509	414
0.4153	12.960	0.0107	1.1505	1.2864	478	0.0107	1.1487	1.2879	477
0.4949	11.864	0.0130	1.2125	1.2079	489	0.0130	1.2135	1.2060	488
0.6097	10.067	0.0175	1.3274	1.1224	464	0.0174	1.3332	1.1173	461
0.6142	9.930	0.0178	1.3326	1.1196	462	0.0177	1.3386	1.1145	459
0.7680	6.969	0.0294	1.5580	1.0444	349	0.0292	1.5631	1.0398	342
0.8933	3.993	0.0572	1.8391	1.0099	189	0.0571	1.8177	1.0083	182
0.9380	2.568	0.0924	1.9724	1.0034	116	0.0924	1.9290	1.0028	111
1.0000	0.251	1.0000	2.1978	1.0000	0	1.0000	2.1057	1.0000	0

Table 2 (Continued)

		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}
Butanone (1) + Hexan-1-ol (2)									
T = 313.15 K									
0.0000	23.702	0.0000	1.0000	2.2672	0	0.0000	1.0000	2.2014	0
0.0594	22.414	0.0021	1.0037	2.0095	117	0.0020	1.0032	1.9797	114
0.1771	20.081	0.0057	1.0299	1.6529	295	0.0057	1.0276	1.6537	290
0.2866	18.221	0.0087	1.0740	1.4376	403	0.0088	1.0706	1.4430	400
0.2970	18.024	0.0090	1.0791	1.4211	411	0.0091	1.0757	1.4264	408
0.4148	16.099	0.0126	1.1482	1.2696	468	0.0126	1.1465	1.2706	467
0.4956	14.601	0.0155	1.2086	1.1939	478	0.0155	1.2098	1.1914	476
0.6094	12.410	0.0208	1.3161	1.1142	451	0.0207	1.3222	1.1086	448
0.6149	12.212	0.0213	1.3221	1.1110	449	0.0212	1.3284	1.1053	445
0.7687	8.477	0.0356	1.5308	1.0410	337	0.0354	1.5355	1.0361	329
0.8937	4.806	0.0701	1.7861	1.0091	182	0.0700	1.7624	1.0074	174
0.9383	3.162	0.1107	1.9061	1.0032	111	0.1106	1.8595	1.0025	106
1.0000	0.369	1.0000	2.1072	1.0000	0	1.0000	2.0106	1.0000	0
T = 323.15 K									
0.0000	35.477	0.0000	1.0000	2.1232	0	0.0000	1.0000	2.0671	0
0.0595	33.537	0.0026	1.0034	1.8972	111	0.0026	1.0030	1.8717	108
0.1775	30.038	0.0072	1.0279	1.5818	280	0.0072	1.0258	1.5823	275
0.2882	27.092	0.0112	1.0691	1.3887	382	0.0113	1.0661	1.3931	379
0.2969	26.920	0.0115	1.0730	1.3765	388	0.0116	1.0700	1.3807	385
0.4158	23.805	0.0164	1.1366	1.2399	441	0.0164	1.1353	1.2403	440
0.4969	21.454	0.0204	1.1914	1.1722	449	0.0203	1.1927	1.1694	447
0.6107	18.139	0.0276	1.2874	1.1013	422	0.0275	1.2930	1.0956	419
0.6150	17.936	0.0280	1.2915	1.0990	421	0.0279	1.2973	1.0933	417
0.7710	12.263	0.0478	1.4766	1.0359	313	0.0476	1.4801	1.0311	305
0.8946	6.885	0.0949	1.6928	1.0080	168	0.0947	1.6699	1.0064	161
0.9391	4.529	0.1498	1.7937	1.0027	103	0.1496	1.7501	1.0021	97
1.0000	0.713	1.0000	1.9591	1.0000	0	1.0000	1.8716	1.0000	0
Butanone (1) + Octan-1-ol (2)									
T = 293.15 K									
0.0000	9.438	0.0000	1.0000	2.9562	0	0.0000	1.0000	2.8544	0
0.0936	8.698	0.0001	1.0122	2.2973	217	0.0001	1.0111	2.2679	211
0.2006	7.978	0.0001	1.0517	1.8352	395	0.0001	1.0485	1.8348	389
0.3150	7.238	0.0002	1.1198	1.5303	516	0.0002	1.1156	1.5334	511
0.3770	6.826	0.0002	1.1674	1.4143	554	0.0002	1.1641	1.4148	550
0.4798	6.191	0.0003	1.2645	1.2710	578	0.0003	1.2652	1.2658	574
0.5597	5.617	0.0003	1.3587	1.1892	565	0.0003	1.3640	1.1808	560
0.6580	4.818	0.0004	1.5052	1.1136	513	0.0004	1.5148	1.1038	505
0.7497	3.943	0.0005	1.6852	1.0619	428	0.0005	1.6911	1.0538	416
0.8049	3.444	0.0007	1.8223	1.0384	359	0.0007	1.8177	1.0322	346
0.9324	1.363	0.0018	2.2689	1.0050	146	0.0018	2.1855	1.0038	137
1.0000	0.003	1.0000	2.6194	1.0000	0	1.0000	2.4352	1.0000	0
T = 298.15 K									
0.0000	12.058	0.0000	1.0000	2.6991	0	0.0000	1.0000	2.6968	0
0.0937	11.092	0.0002	1.0108	2.1629	203	0.0002	1.0108	2.1574	203
0.2009	10.114	0.0003	1.0469	1.7618	373	0.0003	1.0468	1.7592	372
0.3155	9.174	0.0004	1.1112	1.4835	487	0.0004	1.1106	1.4827	486
0.3773	8.633	0.0005	1.1566	1.3754	523	0.0005	1.1560	1.3748	521
0.4801	7.787	0.0006	1.2497	1.2402	544	0.0006	1.2496	1.2389	542
0.5602	7.081	0.0008	1.3392	1.1635	529	0.0008	1.3400	1.1616	527
0.6585	6.044	0.0010	1.4731	1.0944	475	0.0010	1.4751	1.0921	473
0.7501	4.909	0.0013	1.6280	1.0494	392	0.0013	1.6294	1.0474	389
0.8051	4.077	0.0017	1.7385	1.0299	326	0.0017	1.7377	1.0283	323
0.9325	1.641	0.0046	2.0637	1.0036	130	0.0046	2.0440	1.0033	127
1.0000	0.008	1.0000	2.2891	1.0000	0	1.0000	2.2450	1.0000	0
T = 303.15 K									
0.0000	15.309	0.0000	1.0000	2.4984	0	0.0000	1.0000	2.5115	0
0.0937	14.114	0.0002	1.0097	2.0489	191	0.0002	1.0099	2.0487	192
0.2011	12.774	0.0004	1.0427	1.6988	353	0.0004	1.0431	1.6967	353
0.3162	11.512	0.0006	1.1023	1.4475	463	0.0006	1.1025	1.4464	462
0.3777	10.380	0.0007	1.1444	1.3488	496	0.0007	1.1444	1.3482	496
0.4806	9.757	0.0009	1.2315	1.2231	517	0.0009	1.2313	1.2229	516
0.5609	8.809	0.0011	1.3153	1.1512	502	0.0011	1.3152	1.1509	502
0.6591	7.473	0.0015	1.4395	1.0866	451	0.0015	1.4396	1.0862	450
0.7507	6.030	0.0020	1.5808	1.0447	371	0.0020	1.5812	1.0443	370
0.8055	4.982	0.0025	1.6795	1.0268	308	0.0025	1.6796	1.0265	307
0.9327	1.980	0.0070	1.9606	1.0032	122	0.0070	1.9565	1.0031	121
1.0000	0.015	1.0000	2.1468	1.0000	0	1.0000	2.1361	1.0000	0
Butanone (1) + Octan-1-ol (2)									
T = 308.15 K									
0.0000	19.141	0.0000	1.0000	2.4921	0	0.0000	1.0000	2.4538	0
0.0938	17.616	0.0003	1.0104	2.0105	192	0.0003	1.0100	1.9967	189

Table 2 (Continued)

		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}
0.2009	16.039	0.0006	1.0443	1.6579	349	0.0006	1.0429	1.6559	346
0.3161	14.384	0.0009	1.1029	1.4161	453	0.0009	1.1010	1.4161	450
0.3776	13.523	0.0010	1.1429	1.3242	485	0.0010	1.1414	1.3231	482
0.4813	12.059	0.0013	1.2242	1.2082	502	0.0013	1.2248	1.2045	499
0.5618	10.879	0.0016	1.3008	1.1427	487	0.0016	1.3037	1.1374	483
0.6600	9.187	0.0021	1.4136	1.0837	437	0.0021	1.4184	1.0778	431
0.7513	7.290	0.0028	1.5436	1.0447	361	0.0028	1.5458	1.0397	353
0.8060	6.064	0.0036	1.6369	1.0274	301	0.0036	1.6331	1.0236	292
0.9329	2.418	0.0099	1.9174	1.0034	120	0.0099	1.8724	1.0027	114
1.0000	0.025	1.0000	2.1174	1.0000	0	1.0000	2.0232	1.0000	0
					T = 313.15 K				
0.0000	23.702	0.0000	1.0000	2.3991	0	0.0000	1.0000	2.3663	0
0.0939	21.785	0.0004	1.0100	1.9526	187	0.0004	1.0096	1.9406	185
0.2012	19.774	0.0008	1.0426	1.6224	340	0.0008	1.0413	1.6205	337
0.3164	17.771	0.0012	1.0988	1.3945	442	0.0012	1.0971	1.3943	439
0.3780	16.601	0.0015	1.1371	1.3073	472	0.0015	1.1359	1.3062	469
0.4810	14.848	0.0019	1.2142	1.1978	488	0.0019	1.2148	1.1944	485
0.5614	13.335	0.0023	1.2868	1.1355	474	0.0023	1.2894	1.1307	470
0.6613	11.139	0.0031	1.3953	1.0785	424	0.0031	1.3996	1.0731	418
0.7521	8.873	0.0042	1.5166	1.0418	349	0.0042	1.5185	1.0374	341
0.8066	7.297	0.0053	1.6031	1.0256	291	0.0053	1.5995	1.0222	283
0.9330	2.921	0.0147	1.8597	1.0032	116	0.0147	1.8197	1.0025	111
1.0000	0.045	1.0000	2.0404	1.0000	0	1.0000	1.9574	1.0000	0
					T = 323.15 K				
0.0000	35.477	0.0000	1.0000	2.2870	0	0.0000	1.0000	2.2587	0
0.0941	32.555	0.0007	1.0099	1.8629	181	0.0007	1.0096	1.8511	179
0.2017	29.456	0.0014	1.0418	1.5545	327	0.0014	1.0407	1.5519	324
0.3180	26.632	0.0021	1.0957	1.3449	421	0.0021	1.0942	1.3440	418
0.3788	24.531	0.0026	1.1308	1.2677	447	0.0026	1.1297	1.2660	444
0.4822	21.828	0.0033	1.2008	1.1705	459	0.0033	1.2015	1.1665	455
0.5631	19.474	0.0041	1.2651	1.1159	442	0.0041	1.2679	1.1105	437
0.6613	16.365	0.0054	1.3565	1.0676	394	0.0054	1.3609	1.0617	387
0.7544	12.520	0.0077	1.4610	1.0354	321	0.0077	1.4624	1.0305	312
0.8084	10.318	0.0098	1.5321	1.0217	266	0.0097	1.5277	1.0180	257
0.9336	4.117	0.0269	1.7406	1.0027	106	0.0269	1.6986	1.0020	100
1.0000	0.116	1.0000	1.8862	1.0000	0	1.0000	1.8013	1.0000	0

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 5−8

	Redlich−Kister				Wilson		
T/K	A_0	A_1	A_2	$\sigma(P)$/Pa	Λ_{12}	Λ_{21}	$\sigma(P)$/Pa
			Butanone (1) + Hexan-1-ol (2)				
288.15	0.9289	0.0301	0.0871	39	0.6436	0.5307	47
293.15	0.8897	0.0343	0.0487	39	0.6628	0.5425	41
298.15	0.8469	0.0293	0.0399	50	0.6744	0.5648	51
303.15	0.8024	0.0075	0.0276	62	0.6531	0.6204	60
308.15	0.7631	0.0222	0.0466	56	0.7086	0.5998	65
313.15	0.7334	0.0366	0.0485	61	0.7580	0.5786	75
323.15	0.6681	0.0402	0.0446	59	0.8083	0.5860	86
			Butanone (1) + Octan-1-ol (2)				
293.15	0.9475	0.0605	0.0760	51	0.6935	0.4760	53
298.15	0.8750	0.0824	0.0355	30	0.7533	0.4745	27
303.15	0.8182	0.0758	0.0217	45	0.7716	0.5003	42
308.15	0.7818	0.0815	0.0498	56	0.8281	0.4840	57
313.15	0.7482	0.0810	0.0459	60	0.8499	0.4911	61
323.15	0.6801	0.0963	0.0509	149	0.9455	0.4675	144

H^E-experimental data, at 308.15 K. H^E curves obtained from the Reldich-Kister equation give a somewhat worse consistency. In any case, the agreement is reasonable since the quantitative evaluation of H^E from vapor pressures involves considerable uncertainty (Rowlinson, 1982). In the same figure and at the same temperature TS^E curves, obtained from $TS^E = H^E - G^E$, are also plotted. Presumably, the strongly positive entropy is associated with a large gain in configurational freedom on breaking hydrogen bonds due to the favorable specific interaction between the hydroxyl hydrogen and the oxygen of the carbonyl group. Another positive contribution due to the destruction of the strong ketoxy-to-ketoxy interactions by the alkyl chain of the alcohol will increase as the hydrocarbon chain of the alcohol molecule becomes larger.

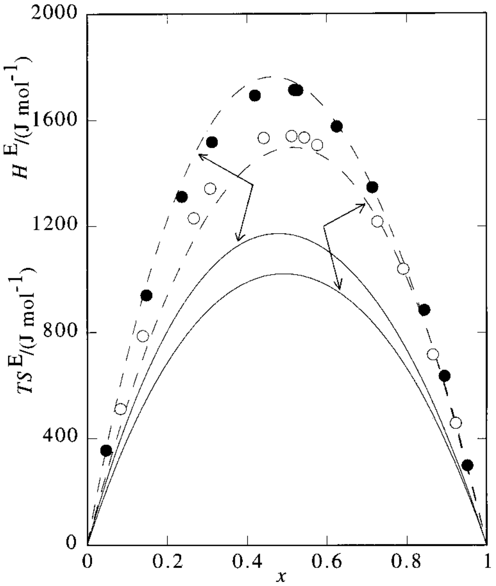

Figure 3. Thermodynamic excess functions, at 308.15 K: H^E-experimental values (Iñarrea *et al.*, 1988) for (○) $(1 - x)C_4H_8O + xC_6H_{13}OH$ and for (●) $(1 - x)C_4H_8O + xC_8H_{17}OH$; (---) H^E-calculated values from Wilson correlation; (—) TS^E values.

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