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Excess Gibbs Free Energies at Eight Temperatures and Excess Enthalpies and Volumes at $T = 298.15$ K for Butanenitrile + 2-Butanol

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Vapor pressures of butanenitrile + 2-butanol at eight temperatures between 278.15 K and 323.15 K were measured by a static method. Excess molar enthalpies and volumes were also measured at $T =$ 298.15 K. Reduction of the vapor pressures to obtain activity coefficients and excess molar Gibbs free energies was carried out by fitting the vapor pressure data to the Redlich−Kister and Wilson correlations according to Barker's method. Azeotropic mixtures with a minimum boiling temperature were observed over the whole temperature range.

Introduction

Following our thermodynamic study of binary mixtures of alcohol + a second polar component (Garriga *et al.*, 1996a−e), we report here vapor pressures at eight temperatures T between 278.15 K and 323.15 K as well as excess enthalpies and volumes at $T = 298.15$ K of (butanenitrile + 2-butanol). Previous measurements of these properties on these mixtures were not found in the literature.

Experimental Section

Butanenitrile and 2-butanol were Fluka products (mole fraction >0.99). 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) except for experimental details which 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. The cell containing the liquid mixture was built of a Young valve (POR/LN/6 type) with a glass plunger consisting of a combination of toric joints of PTFE and Viton; an inner Teflon-covered iron piece served for magnetic stirring. 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 ±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.

Excess enthalpies were measured with a calorimeter working at constant pressure and in the absence of vapor phase (Gutiérrez Losa and Gracia, 1971). The precision of this apparatus is estimated to be about 1% of the maximum value of H^E. A densimeter (Anton Paar DMA 60/DMA 602) was used for density measurements on the pure liquids and mixtures. Uncertainty in density measurements is estimated to be less than 0.000 01 g·cm^{-3}. The temperature was measured by means of a digital thermometer with a Pt sensor, precision 0.01 K. For both excess enthalpy and volume the masses of both components were determined by weighing and the uncertainties in the mole fractions are estimated to be less than 0.0003.

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

	butanenitrile			butan-2-ol		
T/K	V^o/ cm^3·mol^{-1} [a]	P^o/kPa this work	P^o/kPa lit.[b]	V^o/ cm^3·mol^{-1} [c]	P^o/kPa this work	P^o/kPa lit.[d]
278.15	86.25	0.825		90.47	0.508	0.503
283.15		1.132			0.761	0.755
288.15	86.88	1.527		91.38	1.115	1.110
293.15	87.36	2.035		91.86	1.632	1.606
298.15	87.87	2.689		92.35	2.306	2.284
303.15	88.42	3.493	3.476	92.84	3.237	3.198
308.15	88.96	4.486	4.481	93.34	4.440	4.412
313.15	89.57	5.716	5.721	93.86	6.046	6.003
318.15		7.235	7.239		8.093	8.062
323.15	90.66	9.013	9.080	94.92	10.720	10.691

[a] TRC (1960), Timmermans (1950). [b] Marsh *et al.* (1989). [c] TRC (1966). [d] Ambrose and Ghiassee (1987).

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 butanenitrile ($B_{11} = -4120$ cm^3·mol^{-1}) was calculated from the Tsonopoulos (1974) correlation with critical constants and the acentric factor taken from Reid *et al.* (1987) and the dipole moment from McClelland (1963). For 2-butanol $B_{22} = -2640$ cm^3·mol^{-1} was obtained by extrapolation from the Dymond and Smith (1980) compilation, which is favorably compared with the value ($B_{22} = -2720$ cm^3·mol^{-1}) obtained from the Tsonopoulos correlation with constants taken from Reid *et al.* (1987). The mixed virial coefficients were calculated from

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

Vapor pressures of the pure 2-butanol, at ten temperatures (Table 1), were fitted to an Antoine equation

2-Butanol:

$$\ln(P/\mathrm{kPa}) = 15.434086 - \frac{3103.046}{T/\mathrm{K} - 85.580} \qquad (2)$$

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Vapor pressures obtained from eq 2 show a standard deviation of 7 Pa and a maximum deviation of 9 Pa at $T = 303.15$ K. For butanenitrile the experimental data were fitted elsewhere (Garriga *et al.*, 1995).

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 correlation. Similar results were obtained with the Wilson (1964) correlation. The activity coefficients are given by

Redlich−Kister:

$$\ln \gamma_1 = x^2\left[A_0 + \sum_{f=1}^{m}\{A_f(1-2x)^f + 2fA_f(1-x)(1-2x)^{f-1}\}\right] \quad (3)$$

$$\ln \gamma_2 = (1-x)^2\left[A_0 + \sum_{f=1}^{m}\{A_f(1-2x)^f - 2fA_f x(1-2x)^{f-1}\}\right] \quad (4)$$

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

Wilson:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (5)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (6)$$

x_2 being the mole fraction of alcohol.

The vapor pressure is then given by

$$P_{\text{calc}} = x_1\gamma_1 P_1^{\circ} R_1 + x_2\gamma_2 P_2^{\circ} R_2 \quad (7)$$

using for nonideality of the vapor phase the corrections

$$R_1 = \exp\{[(V_1^{\circ} - B_{11})(P - P_1^{\circ}) - P\delta_{12}y_2^{\,2}]/RT\} \quad (8)$$

$$R_2 = \exp\{[(V_2^{\circ} - B_{22})(P - P_2^{\circ}) - P\delta_{12}y_1^{\,2}]/RT\} \quad (9)$$

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

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (10)$$

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 3−6 together with the standard deviations defined by

$$\sigma(P) = \left[\sum_{i=1}^{N}(\delta P)_i^{\,2}/(N-m)\right]^{1/2} \quad (11)$$

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, the vapor-pressure data are somewhat better represented by the Redlich−Kister polynomial. G^E curves are shown in Figure 2, and a negative temperature coefficient can be observed. Excess Gibbs energies show maxima of approximately 910 J·mol^{-1} at 278.15 K and 630 J·mol^{-1} at 323.15 K, at $x \approx 0.5$. We have carried out vapor-pressure measurements using 2-butanol from two sources (Fluka and Aldrich), such as is noted

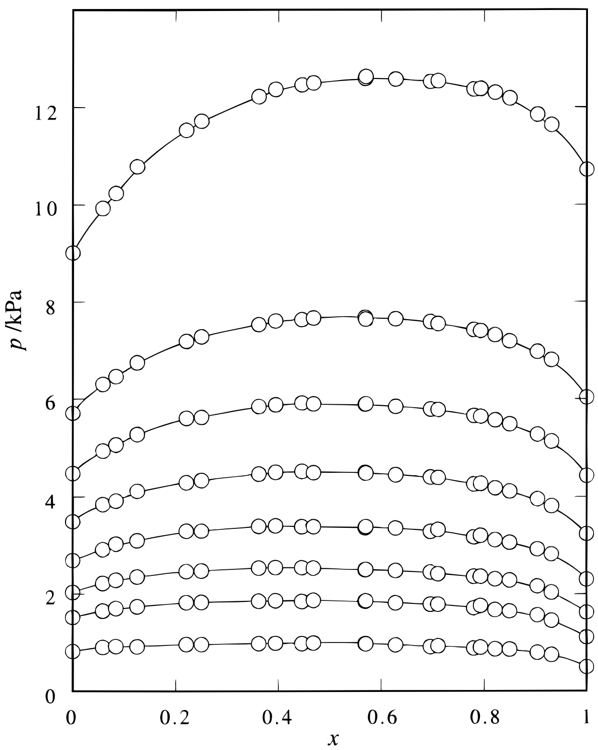

Figure 1. Vapor pressures of $(1 - x)C_4H_7N + x2\text{-}C_4H_9OH$, at T = 278.15, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15 K.

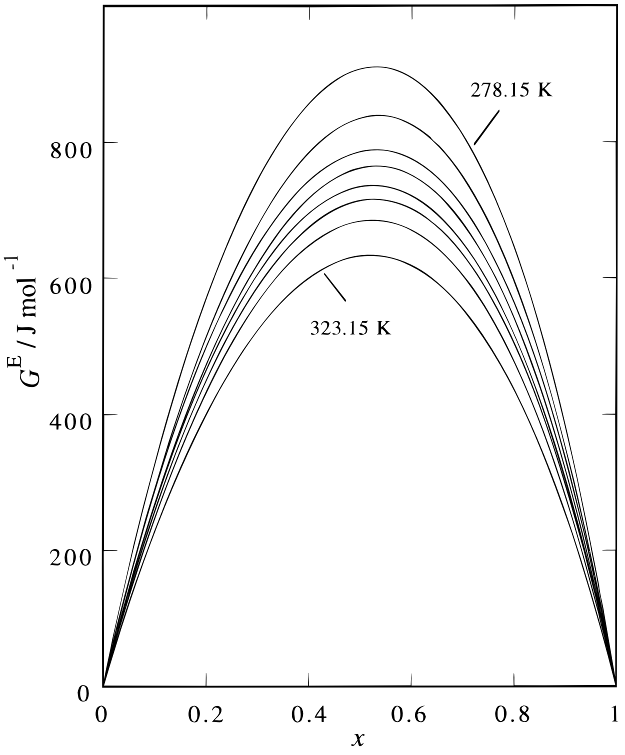

Figure 2. Excess molar Gibbs energies G^E of $(1 - x)C_4H_7N$ + $x2\text{-}C_4H_9OH$ at T = 278.15, 288.15, 293, 298.15, 303.15, 308.15, 313.15, and 323.15 K.

Table 2. Experimental Vapor-Pressure Data, Vapor-Phase Composition, Activity Coefficients, and Excess Molar Gibbs Energy Calculated from the Redlich–Kister Correlation for C_4H_7N (1) + 2-C_4H_9OH (2)

x_2	P/kPa	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}
278.15 K											
0.0000	0.825	0.0000	1.0000	4.9882	0	0.5702^a	0.981	0.4159	1.5781	1.4082	905
0.0589	0.909	0.1309	1.0068	3.9753	203	0.6284^a	0.961	0.4360	1.7539	1.3123	878
0.0842^a	0.927	0.1684	1.0135	3.6463	280	0.6963^a	0.924	0.4659	2.0363	1.2164	815
0.1255	0.925	0.2210	1.0288	3.2067	396	0.7108	0.943	0.4591	2.1113	1.1980	797
0.2206	0.971	0.2895	1.0829	2.5058	612	0.7803^a	0.891	0.4987	2.5738	1.1200	685
0.2500^a	0.967	0.3087	1.1047	2.3483	666	0.7928	0.909	0.4909	2.6800	1.1078	660
0.3618	0.988	0.3539	1.2121	1.9012	822	0.8215^a	0.876	0.5156	2.9590	1.0819	597
0.3944^a	0.997	0.3623	1.2521	1.8025	852	0.8497	0.868	0.5271	3.2910	1.0595	528
0.4459	0.984	0.3838	1.3255	1.6662	888	0.9038^a	0.804	0.5859	4.1498	1.0257	370
0.4685^a	1.000	0.3840	1.3624	1.6127	898	0.9311	0.756	0.6343	4.7371	1.0136	277
0.5696	0.984	0.4146	1.5765	1.4093	905	1.0000	0.508	1.0000	6.9711	1.0000	0
288.15 K											
0.0000	1.527	0.0000	1.0000	3.9028	0	0.5702^a	1.867	0.4640	1.4944	1.3617	835
0.0589	1.657	0.1301	1.0052	3.2814	179	0.6284^a	1.824	0.4905	1.6469	1.2762	811
0.0842^a	1.713	0.1682	1.0104	3.0682	249	0.6964^a	1.792	0.5161	1.8882	1.1905	753
0.1255	1.745	0.2224	1.0225	2.7725	353	0.7108	1.797	0.5180	1.9509	1.1742	737
0.2206	1.827	0.3056	1.0661	2.2682	552	0.7803^a	1.721	0.5587	2.3324	1.1050	632
0.2500^a	1.835	0.3265	1.0841	2.1480	603	0.7929	1.765	0.5482	2.4190	1.0941	609
0.3618	1.861	0.3879	1.1750	1.7888	751	0.8215^a	1.681	0.5839	2.6414	1.0714	551
0.3944^a	1.872	0.4009	1.2095	1.7057	781	0.8498	1.656	0.6019	2.9032	1.0517	486
0.4459	1.853	0.4264	1.2734	1.5888	815	0.9038^a	1.571	0.6560	3.5569	1.0222	340
0.4685^a	1.879	0.4291	1.3057	1.5423	826	0.9312	1.463	0.7182	3.9925	1.0117	254
0.5696	1.857	0.4662	1.4931	1.3626	836	1.0000	1.115	1.0000	5.5645	1.0000	0
293.15 K											
0.0000	2.035	0.0000	1.0000	3.8677	0	0.5702^a	2.504	0.4939	1.4518	1.3279	785
0.0589	2.230	0.1363	1.0060	3.1601	179	0.6284^a	2.481	0.5189	1.5810	1.2544	762
0.0842^a	2.288	0.1760	1.0119	2.9287	247	0.6964^a	2.452	0.5470	1.7862	1.1790	709
0.1255	2.349	0.2284	1.0252	2.6184	348	0.7108	2.414	0.5599	1.8397	1.1644	693
0.2206	2.466	0.3099	1.0710	2.1212	535	0.7803^a	2.365	0.5933	2.1686	1.1012	598
0.2500^a	2.476	0.3313	1.0891	2.0090	581	0.7929	2.362	0.5980	2.2439	1.0910	576
0.3618	2.533	0.3941	1.1751	1.6892	713	0.8216^a	2.308	0.6218	2.4389	1.0695	522
0.3944^a	2.549	0.4089	1.2063	1.6181	739	0.8498	2.284	0.6385	2.6687	1.0508	462
0.4459	2.546	0.4346	1.2626	1.5192	769	0.9038^a	2.166	0.6963	3.2518	1.0221	325
0.4685^a	2.534	0.4469	1.2907	1.4801	778	0.9312	2.035	0.7560	3.6457	1.0117	243
0.5696	2.496	0.4953	1.4507	1.3287	785	1.0000	1.632	1.0000	5.0966	1.0000	0
298.15 K											
0.0000	2.689	0.0000	1.0000	3.3797	0	0.5702^a	3.392	0.5081	1.4294	1.3087	761
0.0589	2.914	0.1345	1.0048	2.8828	166	0.6284^a	3.357	0.5345	1.5561	1.2366	738
0.0842^a	3.025	0.1742	1.0095	2.7111	230	0.6964^a	3.290	0.5688	1.7531	1.1639	685
0.1255	3.098	0.2311	1.0205	2.4716	326	0.7108	3.328	0.5672	1.8036	1.1500	669
0.2206	3.293	0.3186	1.0599	2.0601	508	0.7804^a	3.173	0.6193	2.1076	1.0907	574
0.2500^a	3.296	0.3435	1.0761	1.9613	554	0.7929	3.201	0.6184	2.1750	1.0814	553
0.3618	3.393	0.4099	1.1565	1.6649	687	0.8216^a	3.114	0.6466	2.3486	1.0618	500
0.3944^a	3.406	0.4267	1.1866	1.5960	714	0.8498	3.062	0.6693	2.5492	1.0448	441
0.4459	3.392	0.4550	1.2419	1.4988	745	0.9038^a	2.926	0.7266	3.0421	1.0193	308
0.4685^a	3.386	0.4664	1.2697	1.4600	754	0.9312	2.822	0.7691	3.3640	1.0101	230
0.5696	3.364	0.5120	1.4283	1.3095	761	1.0000	2.306	1.0000	4.4924	1.0000	0
303.15 K											
0.0000	3.493	0.0000	1.0000	3.3200	0	0.5702^a	4.490	0.5282	1.4106	1.2833	731
0.0588	3.845	0.1390	1.0050	2.8061	165	0.6284^a	4.453	0.5571	1.5257	1.2179	708
0.0842^a	3.920	0.1830	1.0100	2.6304	228	0.6965^a	4.412	0.5893	1.7033	1.1516	655
0.1253	4.120	0.2355	1.0214	2.3903	322	0.7107	4.398	0.5965	1.7480	1.1391	641
0.2205	4.298	0.3299	1.0616	1.9846	498	0.7804^a	4.265	0.6431	2.0194	1.0845	549
0.2500^a	4.342	0.3525	1.0778	1.8891	542	0.7927	4.278	0.6461	2.0783	1.0761	529
0.3617	4.472	0.4220	1.1564	1.6095	668	0.8216^a	4.185	0.6729	2.2332	1.0578	478
0.3944^a	4.513	0.4378	1.1852	1.5455	692	0.8496	4.120	0.6964	2.4091	1.0421	422
0.4459	4.529	0.4647	1.2375	1.4562	720	0.9039^a	3.960	0.7529	2.8452	1.0181	294
0.4685^a	4.502	0.4792	1.2634	1.4208	728	0.9311	3.814	0.7983	3.1253	1.0096	220
0.5696	4.505	0.5263	1.4096	1.2841	731	1.0000	3.237	1.0000	4.1096	1.0000	0
308.15 K											
0.0000	4.486	0.0000	1.0000	3.1241	0	0.5702^a	5.909	0.5457	1.3871	1.2718	712
0.0587	4.941	0.1408	1.0047	2.6682	159	0.6284^a	5.852	0.5774	1.4956	1.2094	689
0.0842^a	5.068	0.1853	1.0094	2.5102	221	0.6965^a	5.802	0.6116	1.6630	1.1459	639
0.1252	5.281	0.2417	1.0201	2.2945	311	0.7107	5.790	0.6188	1.7050	1.1339	624
0.2204	5.610	0.3362	1.0578	1.9255	482	0.7804^a	5.664	0.6625	1.9596	1.0815	535
0.2500^a	5.632	0.3626	1.0732	1.8376	525	0.7927	5.650	0.6694	2.0148	1.0734	516
0.3617	5.853	0.4338	1.1471	1.5788	648	0.8217^a	5.574	0.6917	2.1601	1.0557	466
0.3944^a	5.889	0.4523	1.1744	1.5191	672	0.8496	5.493	0.7154	2.3236	1.0407	412
0.4458	5.928	0.4800	1.2235	1.4353	699	0.9039^a	5.281	0.7739	2.7286	1.0175	287
0.4685^a	5.909	0.4942	1.2481	1.4019	707	0.9311	5.136	0.8130	2.9877	1.0093	215
0.5696	5.905	0.5458	1.3861	1.2725	712	1.0000	4.440	1.0000	3.8920	1.0000	0

Table 2 (Continued)

x_2	P/kPa	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}
					313.15 K						
0.0000	5.716	0.0000	1.0000	2.9338	0	0.5702^a	7.653	0.5636	1.3671	1.2491	680
0.0587	6.314	0.1423	1.0044	2.5315	153	0.6283^a	7.657	0.5920	1.4675	1.1913	658
0.0840^a	6.471	0.1877	1.0088	2.3914	212	0.6962^a	7.598	0.6240	1.5944	1.1409	617
0.1251	6.759	0.2459	1.0188	2.1965	299	0.7107	7.558	0.6387	1.6585	1.1217	594
0.2204	7.198	0.3445	1.0548	1.8587	464	0.7802^a	7.433	0.6825	1.8850	1.0739	508
0.2498^a	7.293	0.3686	1.0693	1.7779	505	0.7927	7.414	0.6903	1.9343	1.0664	489
0.3616	7.543	0.4460	1.1400	1.5365	622	0.8214^a	7.327	0.7129	2.0601	1.0505	441
0.3942^a	7.614	0.4642	1.1660	1.4806	645	0.8496	7.199	0.7405	2.2032	1.0367	389
0.4458	7.643	0.4952	1.2130	1.4019	671	0.9037^a	6.982	0.7957	2.5469	1.0158	271
0.4684^a	7.677	0.5065	1.2362	1.3707	678	0.9311	6.817	0.8334	2.7655	1.0083	203
0.5696	7.689	0.5607	1.3662	1.2497	680	1.0000	6.046	1.0000	3.5055	1.0000	0
					323.15 K						
0.0000	9.013	0.0000	1.0000	2.6046	0	0.5701^a	12.635	0.5894	1.3285	1.2163	628
0.0586	9.937	0.1450	1.0038	2.2953	140	0.6283^a	12.579	0.6251	1.4165	1.1652	606
0.0839^a	10.239	0.1918	1.0076	2.1846	195	0.6962^a	12.530	0.6648	1.5470	1.1141	558
0.1246	10.787	0.2513	1.0162	2.0294	275	0.7107	12.543	0.6720	1.5797	1.1043	545
0.2202	11.539	0.3579	1.0481	1.7485	429	0.7802^a	12.376	0.7195	1.7674	1.0629	464
0.2495^a	11.724	0.3836	1.0610	1.6801	467	0.7927	12.384	0.7261	1.8075	1.0564	447
0.3613	12.226	0.4666	1.1248	1.4708	576	0.8214^a	12.304	0.7475	1.9087	1.0428	403
0.3940^a	12.376	0.4859	1.1483	1.4215	598	0.8496	12.190	0.7715	2.0221	1.0310	354
0.4456	12.463	0.5190	1.1908	1.3519	621	0.9037^a	11.856	0.8289	2.2879	1.0133	246
0.4682^a	12.500	0.5326	1.2117	1.3242	628	0.9311	11.644	0.8640	2.4527	1.0070	184
0.5695	12.595	0.5909	1.3276	1.2168	628	1.0000	10.720	1.0000	2.9908	1.0000	0

[a] In these mixtures, 2-butanol was Aldrich quality, low water content, purity (mole fraction) >0.99+.

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 3−6

	Redlich−Kister				Wilson		
T/K	A_0	A_1	A_2	$\sigma(P)$/ Pa	Λ_{12}	Λ_{21}	$\sigma(P)$/ Pa
278.15	1.5690	−0.1674	0.2054	12	0.2324	0.4750	11
288.15	1.3951	−0.1774	0.1439	14	0.2704	0.5633	14
293.15	1.2903	−0.1380	0.2003	12	0.3146	0.5866	16
298.15	1.2300	-0.1423	0.1301	20	0.3298	0.6212	20
303.15	1.1660	−0.1067	0.1406	18	0.3760	0.6157	22
308.15	1.1151	−0.1099	0.1339	20	0.3838	0.6480	25
313.15	1.0511	−0.0890	0.1143	20	0.4226	0.6560	27
323.15	0.9422	−0.0691	0.0842	37	0.4747	0.6883	43

Table 4. Excess Molar Enthalpies and Volumes at 298.15 K

x	H^E/ J·mol^{-1}	x	H^E/ J·mol^{-1}	x	V^E/ cm^3·mol^{-1}	x	V^E/ cm^3·mol^{-1}
0.0955	696	0.5334	1977	0.0479	0.0003	0.8380	0.0027
0.1437	1011	0.5831	1953	0.1083	0.0009	0.9034	0.0013
0.2196	1337	0.5854	1961	0.2156	0.0026	0.9303	0.0006
0.2557	1476	0.6764	1806	0.3411	0.0055		
0.3084	1682	0.7671	1462	0.4267	0.0064		
0.3768	1867	0.8756	963	0.5195	0.0066		
0.4243	1938	0.9246	657	0.5768	0.0061		
0.4510	1970	0.9298	616	0.6805	0.0049		

$$H^E/\text{J·mol}^{-1} = x(1-x)\{7942 - 506(1-2x) + 865(1-2x)^2\};\ \sigma(H^E) = 23$$

$$V^E/\text{cm}^3\text{·mol}^{-1} = x(1-x)\{0.0262 - 0.0026(1-2x) - 0.0231(1-2x)^2\};\ \sigma(V^E) = 0.0003$$

at the bottom of Table 2. The agreement between both sets of data is very good.

Experimental excess molar enthalpies and volumes, at $T = 298.15$ K, are given in Table 4. The results have been fitted to a polynomial

$$Q^E = x(1-x)\sum_{j=0}^{2} A_j(1-2x)^j \qquad (12)$$

where Q^E stands for H^E or V^E and x is the mole fraction of alcohol.

Table 5. Azeotropic Pressures and Mole Fractions

	experimental values			
T/K	x_z	P_z/kPa	x_z eq 13	P_z/kPa eq 15
278.15	0.327	0.978	0.331	0.974
288.15	0.397	1.789	0.395	1.848
293.15	0.430	2.547	0.427	2.505
298.15	0.461	3.388	0.459	3.361
303.15	0.489	4.503	0.491	4.465
308.15	0.524	5.907	0.523	5.878
313.15	0.554	7.687	0.555	7.670
323.15	0.617	12.590	0.619	12.742

We have tested the consistency of the enthalpies and free energies by means of the Gibbs−Helmholtz equation. By fitting $G^E(x)/T$ at round mole fractions with a second-degree polynomial in $1/T$, the derivative gives $H^E(x)$. At $T = 298.15$ K, the H^E-calculated values using $G^E(x)$ values from both Redlich−Kister and Wilson are similar and are shown as a curve in Figure 3a together with the H^E experimental data, at the same temperature, and the TS^E curve calculated from $TS^E = H^E - G^E$. At $x = 0.5$, the H^E-calculated value is about 15% higher than the experimental one. The agreement may be considered acceptable as the quantitative evaluation of H^E from vapor pressures involves considerable uncertainty (Rowlinson and Swinton, 1982).

Azeotropic mixtures with a minimum boiling temperature were observed over the whole range of temperature. Azeotropic mole fractions x_z (mole fraction of alcohol) were graphically calculated, assuming ideal behavior of the vapor, from the well-known equation $\gamma_1/\gamma_2 = P_2^o/P_1^o$. Azeotropic compositions are linearly related to temperature by means of

$$x_z = a + b(T/K) \qquad (13)$$

where $a = -1.4457$ and $b = 6.388 \times 10^{-3}$.

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

$$\frac{\mathrm{d}\ln P_z}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H_z}{RT^2} \qquad (14)$$

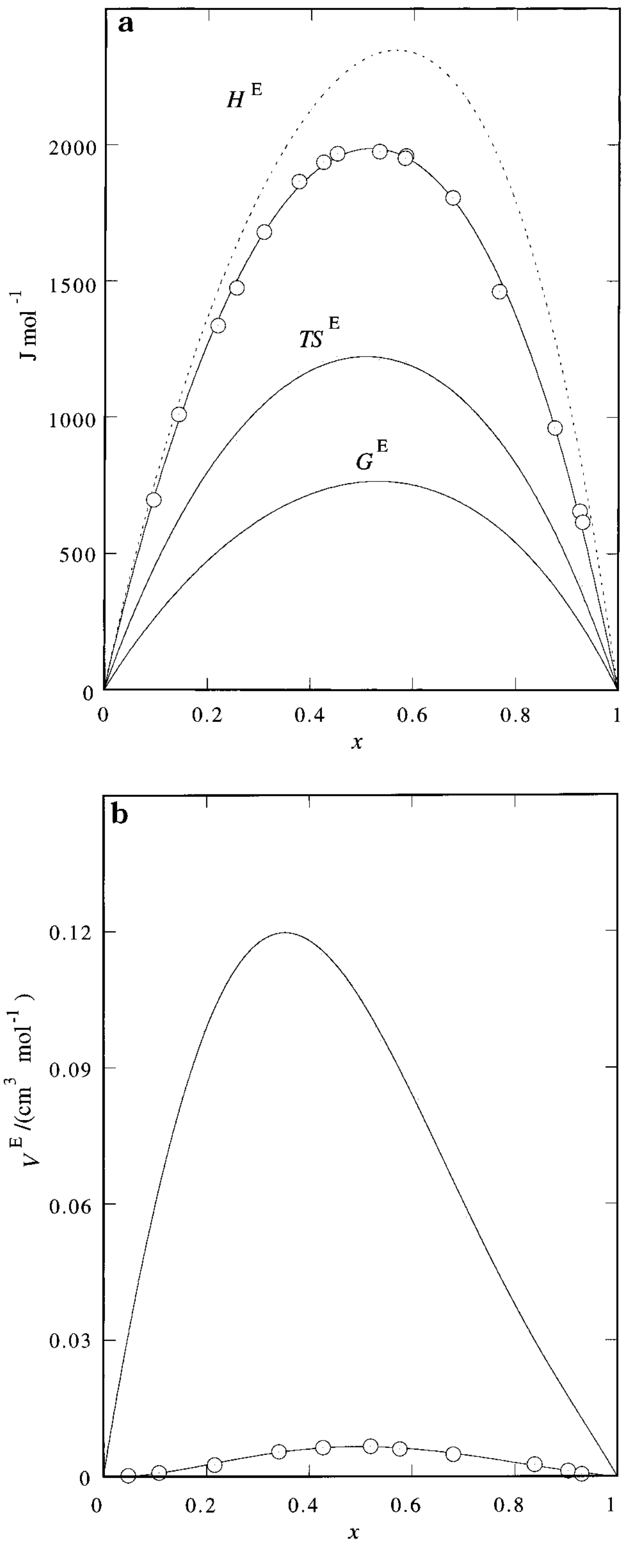

Figure 3. (a) Thermodynamic excess functions, at $T = 298.15$ K: (○) H^E experimental values; (···) H^E calculated from the Gibbs–Helmholtz equation. (b) Excess volumes V^E for (○) $(1 - x)C_4H_7N + x2\text{-}C_4H_9OH$ and (—) $(1 - x)C_4H_7N + x1\text{-}C_4H_9OH$ (Garriga *et al.*, 1995).

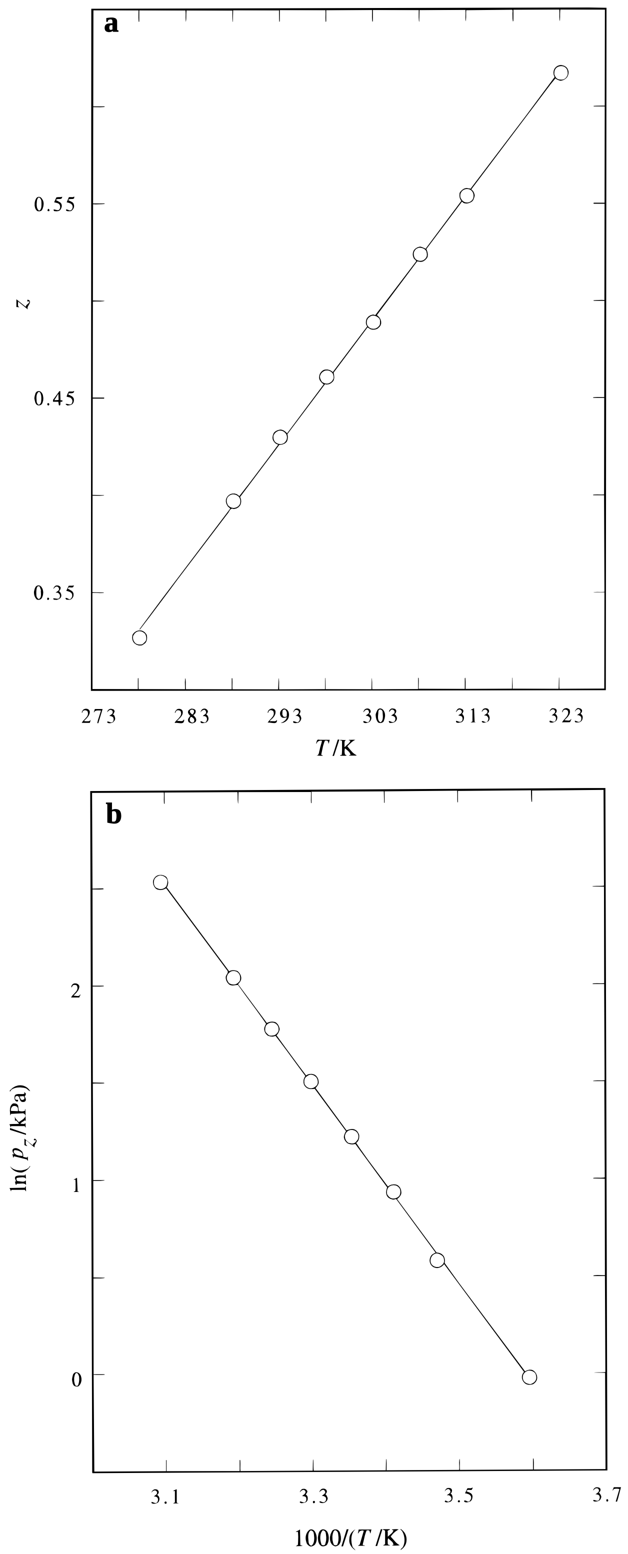

Figure 4. (a) Azeotropic mole fractions and (b) azeotropic vapor pressures.

is satisfied. If we accept that the enthalpy of azeotropic vaporization $\Delta_{vap}H_z$ is constant, the azeotropic pressure is related to the temperature in a way similar to that of a pure substance

$$\ln(P_z/\text{kPa}) = A + \frac{B}{(T/\text{K})} \qquad (15)$$

with $A = 18.44$ and $B = -5136$. Experimental and calculated (from eqs 13 and 15) azeotropic compositions and pressures are compared in Table 5 and plotted in Figure 4.

The behavior of mixtures of an alcohol with butanenitrile as a strong polar solvent (dipole moment $\mu = 1.36 \times 10^{-29}$ C·m) (McClelland, 1963) is controlled by the strong solvent–solvent and hydroxy group–solvent interactions. As a consequence of these interactions the excess molar enthalpies and entropies are much more positive than those for inert solvent in place of butanenitrile. In Table 6, experi-

Table 6. Thermodynamic Excess Functions for {0.5Alkanol + 0.5Butanenitrile, + 0.5Benzene or + 0.5*n*-Hexane}, at 298.15 K

	butanenitrile			benzene[b]			*n*-hexane[b]		
alkanol	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}	H^E/ J·mol^{-1}	TS^E/ J·mol^{-1}	V^E/ cm^3·mol^{-1}
1-butanol	1588[a]	801[a]	0.105[a]	1025	100	0.18	510	−630	0.08
2-butanol	1985	1223	0.007	1590	675	0.46	858	−213[c]	0.439[d]

[a] Garriga *et al.* (1995). [b] Brown *et al.* (1969). [c] Calculated from G^E data from Rodríguez *et al.* (1993). [d] Pardo *et al.* (1992) at $T = 303.15$ K.

mental values of thermodynamic properties of two butanols at $T = 298.15$ K are briefly summarized and compared with solvents which show specific interactions with the hydroxyl group, and including *n*-hexane as inert solvent. Presumably, the strong entropy increase in mixtures with specific interactions is associated with a large gain in configurational freedom on breaking hydrogen bonds. For mixtures containing 2-butanol, H^E and TS^E are noticeably larger than those for mixtures with 1-butanol. On the contrary, V^E is lower for 2-butanol than for 1-butanol. For both isomers, the variation with the composition at $T = 298.15$ K is shown in Figure 3b.

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