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Vapor Pressures at Several Temperatures between 278.15 and 323.15 K and Excess Functions at $T = 298.15$ K for 1-Bromobutane with 1-Butanol or 2-Methyl-2-propanol

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Vapor pressures of (1-bromobutane + 1-butanol or 2-methyl-2-propanol) at several temperatures between 278.15 and 323.15 K were measured by a static method. Excess molar enthalpies and volumes were also measured at 298.15 K. The reduction of the vapor pressures to obtain activity coefficients and excess molar Gibbs energies was carried out by fitting the Redlich−Kister correlation to the vapor pressure data according to Barker's method. Azeotropic mixtures with a minimum boiling temperature were observed over the whole temperature range.

Introduction

Hydrogen bonding plays an important role in both fundamental science and industrial applications. Although many experimental and theoretical studies have been directed toward understanding hydrogen bonding, it remains an area of active research. In previous papers, we have reported vapor−liquid equilibrium (VLE) measurements at several temperatures as well as excess enthalpies and excess volumes at $T = 298.15$ K for binary mixtures of butanol isomers + butanenitrile,[1−4] + butanone,[5−7] + di-*n*-propyl ether,[8,9] and + 1-chlorobutane.[10,11] Thermodynamic data for binary mixtures of an alcohol with a second polar component are necessary for a better understanding of hydrogen bonding and for the development and testing of models and theories of associated systems in the liquid state. We report vapor pressures at eight temperatures for (1-bromobutane + 1-butanol) and at six temperatures for (1-bromobutane + 2-methyl-2-propanol). We have also measured excess enthalpies and excess volumes at $T = 298.15$ K.

Experimental Section

Chemicals. 1-Butanol was supplied by Fluka (mole fraction >0.995). 1-Bromobutane and 2-methyl-2-propanol were Aldrich products (mole fraction >0.990 and >0.995, respectively). All the chemicals had low water content, were stored over a molecular sieve (3A), and were used without further purification. The mass fraction purity was checked by gas−liquid chromatography and found to be 0.996 for 1-bromobutane, 0.999 for 1-butanol, and 0.998 for 2-methyl-2-propanol.

Apparatus and Procedures. The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh,[12] except for some experimental details which have been described previously.[13,14] 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 was 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 <0.0003. Manometric levels were read 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.

A Thermometric 2277 thermal activity monitor, together with two Shimadzu (model LC-10AD) variable speed piston pumps, were used to determine H^E at $T = 298.15$ K. The precision of the H^E measurements is better than ±2%. The accuracy of the method was verified with a test on (benzene + cyclohexane).[15] The experimental results agreed with the literature data to within ±10 J, in the worst case. A densimeter (Anton Paar DMA 60/DMA 602) was used for density measurements on the pure liquids and mixtures. The densimeter works at 298.15 K and the sample density is calculated from the vibration period with an uncertainty of ±0.000 02 $g\cdot cm^{-3}$. The accuracy for V^E is estimated to be 0.002 $cm^3\cdot mol^{-1}$.

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-bromobutane at ten temperatures between 278.15 and 323.15 K (Table 1) were fitted with an Antoine equation

$$\ln(P/\text{kPa}) = 14.12331 - \frac{3088.751}{(T/\text{K}) - 49.418} \qquad (1)$$

Vapor pressures obtained from eq 1 show a standard deviation of 8 Pa and a maximum deviation of −14 Pa at $T = 323.15$ K. For 1-butanol the experimental vapor pressures were fitted previously.[14]

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Table 1. Molar Volumes V^0 and Vapor Pressures P^0 of the Pure Compounds Used in Barker Analysis

	1-bromobutane			1-butanol			2-methyl-2-propanol		
		P^0 (kPa)			P^0 (kPa)			P^0 (kPa)	
T (K)	$V^{0\ a}$ (cm^3·mol^{-1})	b	c	$V^{0\ d}$ (cm^3·mol^{-1})	b	e	$V^{0\ d}$ (cm^3·mol^{-1})	b	e
278.15	105.6*	1.860	1.855	90.3	0.197	0.189			
283.15	106.2*	2.480	2.477	90.7	0.300	0.286			
288.15	106.8	3.265	3.269	91.1	0.453	0.427			
293.15	107.4	4.261	4.264	91.5	0.635	0.625			
298.15	108.0	5.506	5.502	92.0	0.933	0.901	94.9	5.610	5.598
303.15	108.7	7.039	7.027	92.4	1.315	1.280	95.6	7.685	7.661
308.15	109.3*	8.899	8.889	92.8	1.827	1.793	96.2	10.347	10.342
313.15	109.9*	11.148	11.431	93.3	2.518	2.477	96.9	13.787	13.779
318.15	110.5*	13.872	13.851	93.7	3.429	3.380	97.6	18.143	18.134
323.15	111.2*	17.092	17.077	94.2	4.586	4.556	98.3	23.578	23.588

[a] Timmermans[16] (* interpolated values). [b] This work. [c] Riddick.[17] [d] TRC.[18] [e] Ambrose and Ghiassee.[19]

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-Bromobutane (1) + 1-Butanol (2)						
					278.15 K						
0.0306	1.861	3	1.0038	8.0077	156	0.5699	1.591	−27	1.8471	1.2460	900
0.0993	1.859	24	1.0368	4.9920	445	0.6662	1.465	−3	2.1236	1.1428	787
0.1687	1.841	28	1.0990	3.4160	661	0.7395	1.347	32	2.3850	1.0880	668
0.1936	1.828	21	1.1274	3.0438	722	0.7774	1.228	10	2.5471	1.0655	595
0.2908	1.796	6	1.2645	2.1175	889	0.8681	0.918	−8	3.0557	1.0247	390
0.3627	1.764	−8	1.3895	1.7422	950	0.9337	0.608	−21	3.5943	1.0067	211
0.4675	1.700	−19	1.6025	1.4226	962						
					288.15 K						
0.0306	3.294	16	1.0035	7.3318	154	0.5702	2.854	−17	1.8194	1.2296	899
0.0993	3.277	22	1.0345	4.7057	442	0.6663	2.613	0	2.0849	1.1301	783
0.1688	3.244	24	1.0934	3.2829	658	0.7397	2.357	16	2.3288	1.0784	661
0.1937	3.234	26	1.1203	2.9405	720	0.7776	2.192	21	2.4756	1.0577	587
0.2909	3.181	9	1.2516	2.0728	889	0.8682	1.651	−5	2.9152	1.0212	382
0.3628	3.129	−9	1.3723	1.7133	951	0.9337	1.125	−26	3.3543	1.0057	205
0.4676	3.010	−34	1.5800	1.4026	962						
					293.15 K						
0.0306	4.297	10	1.0035	7.0716	154	0.5704	3.709	−33	1.7918	1.2366	906
0.0993	4.285	19	1.0339	4.5723	441	0.6664	3.426	14	2.0522	1.1370	793
0.1688	4.246	24	1.0915	3.2141	658	0.7398	3.080	8	2.2981	1.0839	673
0.1937	4.252	44	1.1177	2.8865	719	0.7777	2.884	24	2.4493	1.0622	600
0.2910	4.169	16	1.2450	2.0536	889	0.8683	2.228	11	2.9160	1.0233	392
0.3629	4.086	−16	1.3613	1.7074	952	0.9338	1.527	−46	3.3992	1.0063	212
0.4677	3.934	−37	1.5607	1.4064	966						
					298.15 K						
0.0305	5.580	28	1.0034	6.8253	153	0.5706	4.852	−16	1.7801	1.2334	911
0.0993	5.588	48	1.0329	4.4664	441	0.6665	4.437	−12	2.0380	1.1344	797
0.1688	5.528	42	1.0889	3.1675	658	0.7399	4.037	23	2.2804	1.0818	676
0.1937	5.513	46	1.1145	2.8515	720	0.7779	3.782	42	2.4288	1.0603	602
0.2911	5.412	17	1.2392	2.0407	892	0.8685	2.905	−9	2.8806	1.0224	393
0.3630	5.285	−42	1.3535	1.7006	956	0.9339	2.048	−44	3.3400	1.0060	212
0.4678	5.109	−50	1.5505	1.4027	971						
					303.15 K						
0.0305	7.146	32	1.0033	6.6084	153	0.5709	6.234	−23	1.7637	1.2333	915
0.0993	7.165	46	1.0322	4.3627	441	0.6667	5.724	−8	2.0177	1.1349	802
0.1688	7.115	58	1.0870	3.1159	658	0.7401	5.192	6	2.2580	1.0823	681
0.1938	7.075	42	1.1122	2.8099	721	0.7782	4.894	51	2.4061	1.0607	607
0.2912	6.930	−8	1.2340	2.0245	893	0.8686	3.816	6	2.8566	1.0226	397
0.3631	6.814	−33	1.3457	1.6929	958	0.9339	2.720	−58	3.3167	1.0061	214
0.4679	6.586	−42	1.5382	1.4007	975						
					308.15 K						
0.0305	9.045	30	1.0033	6.3730	153	0.5713	7.875	−45	1.7366	1.2341	914
0.0993	9.110	64	1.0318	4.2282	439	0.6669	7.234	−30	1.9811	1.1379	804
0.1689	9.057	80	1.0857	3.0362	656	0.7403	6.613	18	2.2170	1.0852	685
0.1938	9.005	58	1.1102	2.7451	717	0.7785	6.271	95	2.3651	1.0632	611
0.2914	8.827	8	1.2288	1.9933	889	0.8689	4.925	5	2.8246	1.0238	401
0.3633	8.642	−52	1.3364	1.6763	954	0.9340	3.565	−92	3.3052	1.0065	218
0.4680	8.345	−56	1.5204	1.3964	971						
					313.15 K						
0.0305	11.366	50	1.0032	6.0721	151	0.5718	9.889	−43	1.7081	1.2262	901
0.0993	11.444	61	1.0312	4.0598	434	0.6671	9.081	−29	1.9386	1.1343	793
0.1689	11.394	86	1.0839	2.9364	648	0.7406	8.277	−4	2.1623	1.0834	675
0.1939	11.335	64	1.1078	2.6603	709	0.7789	7.898	131	2.3034	1.0620	602
0.2916	11.096	−9	1.2230	1.9481	878	0.8691	6.233	−8	2.7408	1.0235	396
0.3635	10.892	−45	1.3266	1.6473	941	0.9341	4.624	−95	3.2010	1.0064	215
0.4682	10.482	−69	1.5024	1.3813	957						
					323.15 K						
0.0304	17.461	44	1.0031	5.5825	149	0.5734	15.389	58	1.6613	1.2109	877
0.0993	17.651	37	1.0301	3.7814	427	0.6677	13.979	−105	1.8676	1.1271	772
0.1690	17.584	49	1.0807	2.7686	636	0.7413	12.848	5	2.0701	1.0795	658
0.1940	17.523	38	1.1036	2.5189	695	0.7800	12.192	115	2.1996	1.0591	586
0.2921	17.217	−7	1.2131	1.8704	859	0.8698	9.847	−21	2.5979	1.0226	386
0.3642	16.888	−57	1.3103	1.5962	919	0.9344	7.647	−51	3.0186	1.0062	210
0.4681	16.273	−48	1.4711	1.3551	934						

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})
1-Bromobutane (1) + 2-Methyl-2-propanol (2)											
298.15 K											
0.0660	7.131	44	1.0158	5.0190	300	0.5941	7.991	20	1.7223	1.2339	856
0.0953	7.386	−10	1.0316	4.2071	409	0.6791	7.837	10	1.9325	1.1555	767
0.1989	7.798	−41	1.1198	2.5904	694	0.7664	7.634	45	2.2459	1.0911	634
0.2914	7.950	−23	1.2294	1.9368	840	0.8276	7.349	5	2.5739	1.0541	512
0.3897	8.053	7	1.3669	1.5743	911	0.9167	6.718	−43	3.3551	1.0146	283
0.5011	8.031	−18	1.5447	1.3502	911						
303.15 K											
0.0695	9.175	29	1.0164	4.6423	307	0.5942	10.488	24	1.7006	1.2242	846
0.0951	9.517	11	1.0297	4.0166	400	0.6791	10.310	3	1.9049	1.1475	757
0.1988	10.102	−56	1.1134	2.5290	682	0.7664	10.085	55	2.2032	1.0855	623
0.2913	10.354	−17	1.2185	1.9098	828	0.8277	9.734	−1	2.5083	1.0504	502
0.3897	10.498	4	1.3518	1.5592	900	0.9168	8.983	−47	3.2149	1.0134	276
0.5010	10.522	−11	1.5261	1.3390	900						
308.15 K											
0.0693	11.636	35	1.0158	4.4272	301	0.5942	13.555	6	1.6727	1.2169	834
0.0948	12.086	6	1.0285	3.8502	393	0.6791	13.395	6	1.8676	1.1428	746
0.1985	12.920	−67	1.1092	2.4598	671	0.7665	13.154	74	2.1512	1.0828	614
0.2911	13.295	−11	1.2105	1.8735	815	0.8278	12.736	−5	2.4397	1.0488	495
0.3896	13.532	30	1.3385	1.5391	886	0.9168	11.860	−58	3.1036	1.0130	272
0.5010	13.572	−24	1.5057	1.3276	887						
313.15 K											
0.0690	14.563	15	1.0148	4.2004	293	0.5941	17.432	15	1.6486	1.2103	824
0.0951	15.221	26	1.0271	3.6701	385	0.6791	17.281	15	1.8380	1.1375	736
0.1986	16.397	−65	1.1037	2.3979	658	0.7664	16.995	62	2.1096	1.0792	606
0.2912	16.924	−13	1.2003	1.8464	802	0.8277	16.541	−7	2.3821	1.0465	487
0.3896	17.273	31	1.3235	1.5254	874	0.9169	15.536	−57	2.9987	1.0123	267
0.5009	17.389	−32	1.4857	1.3193	876						
318.15 K											
0.0693	18.084	6	1.0138	3.9484	285	0.5940	22.161	13	1.6272	1.1986	807
0.0947	18.953	49	1.0250	3.4922	372	0.6791	22.018	2	1.8104	1.1278	720
0.1983	20.581	−77	1.0968	2.3375	641	0.7664	21.761	102	2.0656	1.0724	590
0.2909	21.322	−29	1.1888	1.8184	785	0.8277	21.229	6	2.3134	1.0420	472
0.3894	21.840	38	1.3079	1.5086	857	0.9168	20.033	−102	2.8512	1.0110	257
0.5008	22.062	−31	1.4670	1.3061	860						
323.15 K											
0.0689	22.269	10	1.0129	3.7576	277	0.5940	27.899	−20	1.6033	1.1920	795
0.0941	23.361	42	1.0234	3.3469	362	0.6791	27.808	−28	1.7804	1.1228	709
0.1977	25.595	−83	1.0914	2.2820	627	0.7665	27.608	127	2.0242	1.0690	580
0.2905	26.624	−35	1.1793	1.7914	769	0.8278	27.010	0	2.2576	1.0398	464
0.3891	27.442	129	1.2939	1.4940	843	0.9169	25.711	−87	2.7550	1.0103	252
0.5005	27.699	−70	1.4478	1.2973	847						

The second virial coefficient, at $T = 325.0$ K, of 1-bromobutane ($B_{11} = -1200$ cm^3·mol^{-1}) was taken from Velasco,[20] that of 1-butanol ($B_{22} = -3918$ cm^3·mol^{-1}) was calculated from the Tsonopoulos[21] correlation, and that of 2-methyl-2-propanol ($B_{22} = -1400$ cm^3·mol^{-1}) was calculated by interpolation of values taken from the TRC tables.[22] The mixed virial coefficient was calculated according to a cubic combination rule,

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

Table 2 shows our vapor pressure measurements along with the activity coefficients γ_1 and γ_2 and the excess molar Gibbs energy G^E values fitted by Barker's method[23] to a Redlich−Kister polynomial,

$$G^E/RT = x_1x_2\sum_{j=0}^{2} A_j(x_1 - x_2)^j \tag{3}$$

The activity coefficients are given by

$$\ln\gamma_1 = x_2{}^2\left[A_0 + \sum_{j=1}^{2}\{A_j(x_1 - x_2)^j + 2jA_jx_1(x_1 - x_2)^{j-1}\}\right] \tag{4}$$

$$\ln\gamma_2 = x_1{}^2\left[A_0 + \sum_{j=1}^{2}\{A_j(x_1 - x_2)^j - 2jA_jx_2(x_1 - x_2)^{j-1}\}\right] \tag{5}$$

where the subscripts 1 and 2 stand for 1-bromobutane and alcohol, respectively. The vapor pressure is then given by

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

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

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

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

where V_1^0 and V_2^0 are the molar volumes, y_1 and y_2 are the vapor-phase mole fractions of 1-bromobutane and alcohol, respectively, and δ_{12} is given by

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

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 and mass of the vapor phase. In Table 3, the Redlich−Kister parameters are given, 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

Table 3. Parameters and Standard Deviations $\sigma(P)$ of Eqs 3, 4, 5, and 10

	1-bromobutane (1) + 1-butanol (2)				1-bromobutane (1) + 2-methyl-2-propanol (2)			
T (K)	A_0	A_1	A_2	σ (Pa)	A_0	A_1	A_2	σ (Pa)
278.15	1.6421	0.4233	0.2612	20				
288.15	1.5855	0.4213	0.2149	21				
293.15	1.5665	0.3859	0.2301	27				
298.15	1.5481	0.3771	0.2140	37	1.4702	0.2645	0.3516	34
303.15	1.5295	0.3612	0.2117	38	1.4292	0.2570	0.3158	36
308.15	1.5003	0.3377	0.2263	59	1.3853	0.2475	0.3048	45
313.15	1.4550	0.3283	0.2290	67	1.3460	0.2338	0.2783	43
318.15					1.3006	0.2291	0.2366	64
323.15	1.3750	0.3143	0.2320	60	1.2605	0.2174	0.2152	84

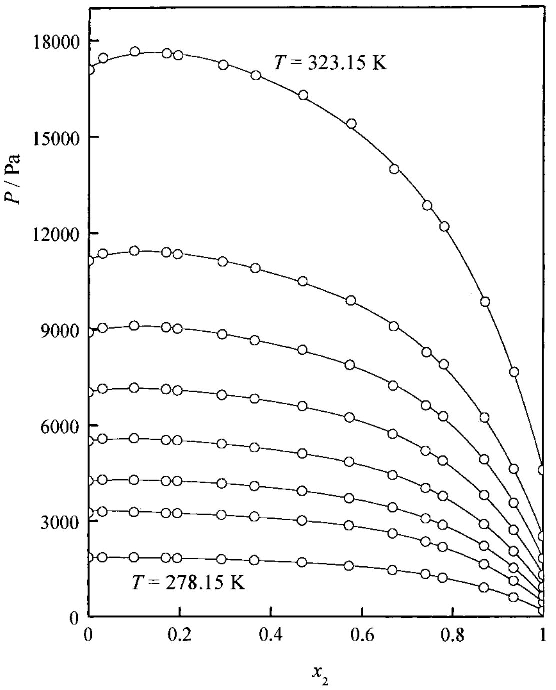


Figure 1. Vapor pressures plotted against liquid-phase composition of alcohol, at working temperatures between 278.15 and 323.15 K, for $\{x_1$ 1-bromobutane + x_2 1-butanol$\}$.

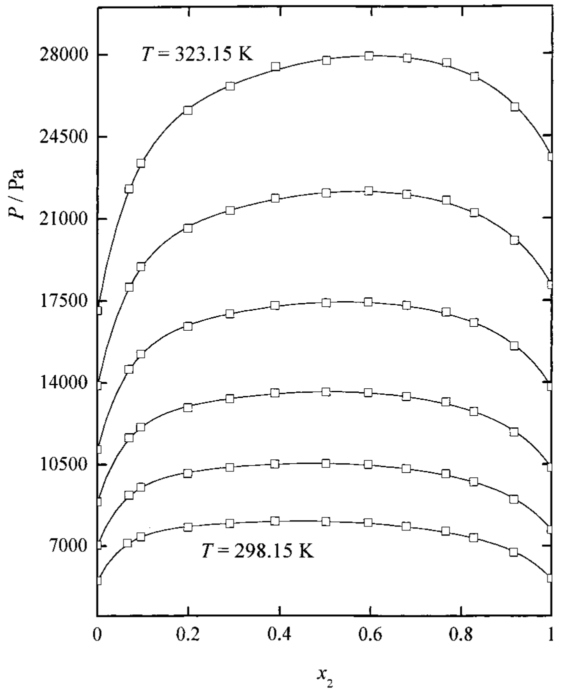


Figure 2. Vapor pressures plotted against liquid-phase composition of alcohol, at working temperatures between 298.15 and 323.15 K, for $\{x_1$ 1-bromobutane + x_2 2-methyl-2-propanol$\}$.

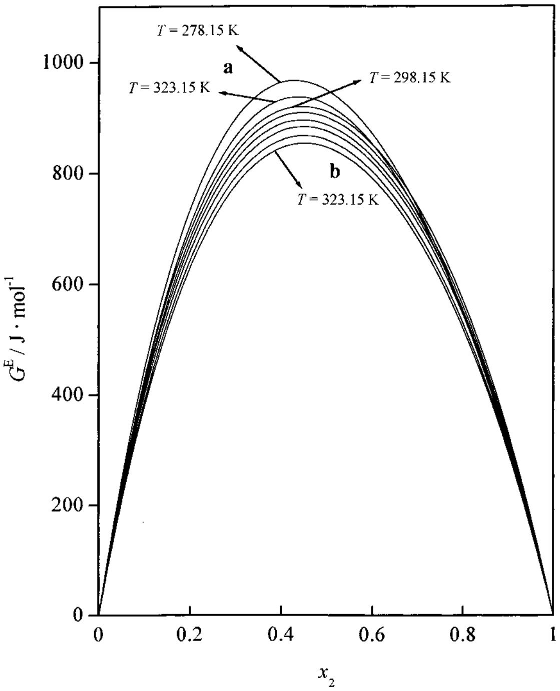


Figure 3. Excess molar Gibbs energies G^E for (a) $\{x_1$ 1-bromobutane + x_2 1-butanol$\}$ at the lowest and highest temperatures and (b) $\{x_1$ 1-bromobutane + x_2 2-methyl-2-propanol$\}$ at all temperatures, plotted as a function of mole fraction of alcohol.

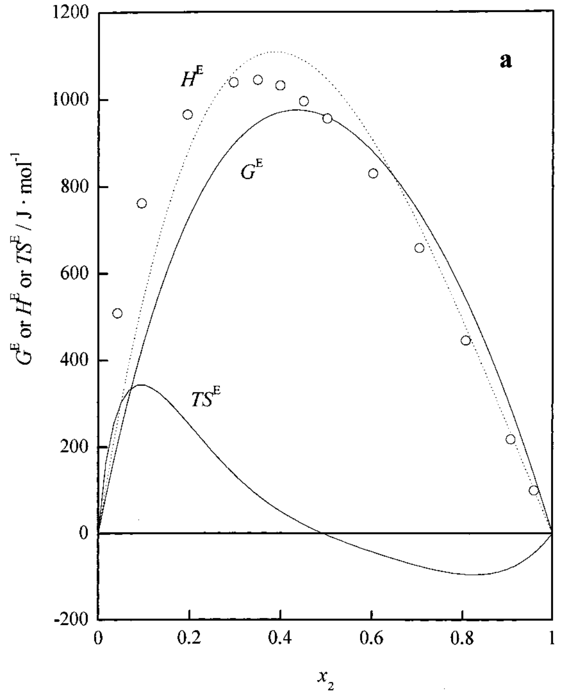
method and N is the number of experimental points. Vapor pressure–liquid composition curves are shown in Figures 1 and 2. For both systems, Figure 3 shows the analytic equations for G^E. For mixtures containing 2-methyl-2-propanol the temperature coefficient is negative in the whole mole fraction range, whereas in the case of 1-butanol a positive coefficient is observed for mixtures rich in alcohol.

Experimental excess molar enthalpies and volumes, at 298.15 K, are given in Table 4 and plotted in Figures 4 and 5. The results were fitted with a polynomial,

$$Q^E = x_1 x_2 \sum_{j=0}^{m} C_j x_2^{j/2} \tag{11}$$

where Q^E denotes H^E or V^E and x_1 and x_2 the mole fractions of 1-bromobutane and alcohol, respectively. For alcoholic mixtures, this polynomial[25,26] represents the experimental behavior better than the classical Redlich–Kister equation. Table 5 gives the C_j coefficients along with the standard deviations.

We test the consistency of the enthalpies and free energies by means of the Gibbs–Helmholtz equation. The coefficients $\partial A_j/\partial T$ have been obtained by fitting the Redlich–Kister parameters A_j to a linear function of the tempera-



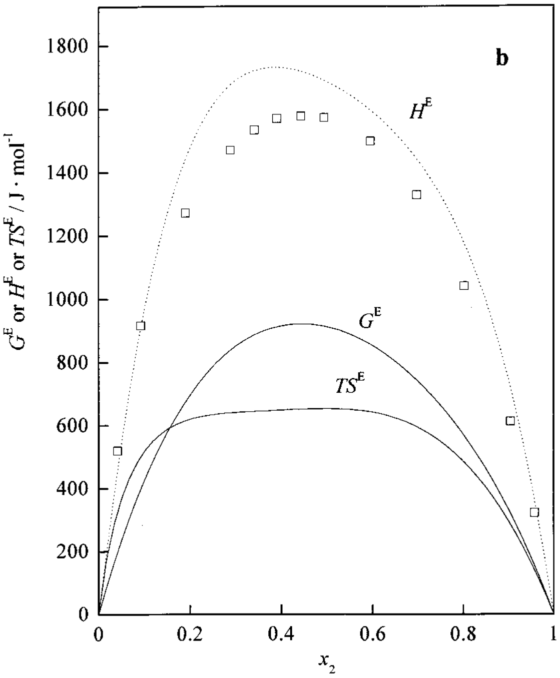


Figure 4. Thermal excess molar functions, at $T = 298.15$ K: (a) {x_1 1-bromobutane + x_2 1-butanol}, ○, experimental H^E; (b) {x_1 1-bromobutane + x_2 2-methyl-2-propanol}, □, experimental H^E. ···, Gibbs−Helmholtz H^E, and —, G^E and TS^E.

ture. The H^E-calculated values, at $T = 298.15$ K, are shown as curves in Figure 4 together with the H^E-experimental data. The agreement is reasonable considering that the quantitative evaluation of H^E from vapor pressures involves considerable uncertainty.[27] In the same figure and at the same temperature, TS^E curves, obtained from $TS^E = H^E - G^E$, are also plotted.

For both systems, azeotropic mixtures with a minimum boiling temperature were observed over the whole range of temperature. Azeotropic mole fractions z_2 were graphically calculated, assuming ideal behavior of the vapor, from the well-known equation, $\gamma_1/\gamma_2 = P_2^0/P_1^0$. Azeotropic compositions show a linear relation with the tempera-

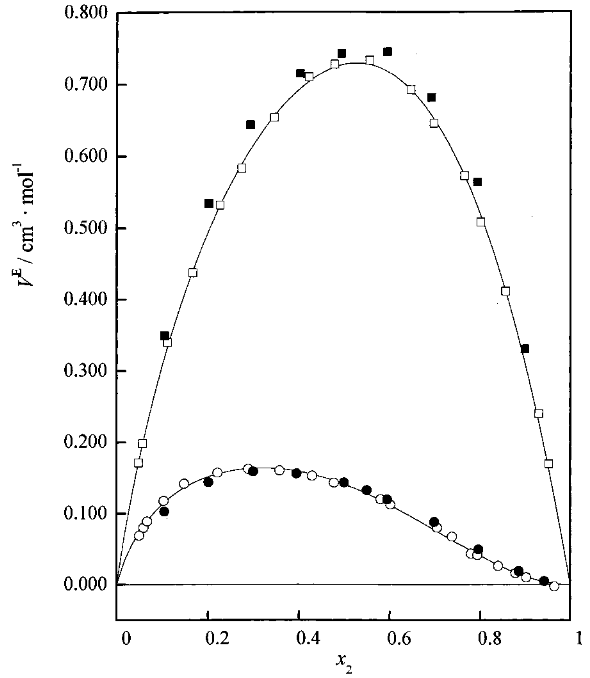


Figure 5. Excess molar volumes, at $T = 298.15$ K: ○, {x_1 1-bromobutane + x_2 1-butanol}; □, {x_1 1-bromobutane + x_2 2-methyl-2-propanol}. ●, ■, Artigas et al.[24].

ture according to the equation

$$z_2 = a + b(T/\mathrm{K}) \tag{12}$$

For 1-bromobutane + 1-butanol $a = -0.5313$ and $b = 1.960 \times 10^{-3}$ K^{-1}, and for 1-bromobutane + 2-mehtyl-2-propanol $a = -0.4098$ and $b = 6.240 \times 10^{-3}$ K^{-1}.

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

$$\mathrm{d}\ln P_z/\mathrm{d}T = \Delta_{\mathrm{vap}}H_z/RT^2 \tag{13}$$

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

$$\ln(P_z/\mathrm{Pa}) = A + B(T/\mathrm{K})^{-1} \tag{14}$$

For 1-bromobutane + 1-butanol $A = 23.71$ and $B = -4497$ K, and for 1-bromobutane + 2-mehtyl-2-propanol $A = 25.05$ and $B = -4787$ K. Experimental and calculated (from eqs 12 and 14) azeotropic compositions and pressures are compared in Table 6.

In Table 7, experimental values of thermodynamic properties are briefly summarized at $T = 298.15$ K for butanol isomers with solvents of different polarity including n-hexane as an inert solvent.

In mixtures of an alcohol with a polar solvent, the excess molar enthalpies and entropies are much more positive than those of n-hexane in place of a polar solvent, as shown in Table 7. When the solvent polarity is increased, both properties increase as more hydrogen bonds are broken at a given mole fraction due to the stronger hydroxyl-group-solvent interaction.

As is well-known, with the same solvent all excess functions are more positive in mixtures containing 2-methyl-2-propanol, particularly TS^E and H^E, which suggests that

Table 4. Experimental Molar Excess Enthalpies and Excess Volumes at $T = 298.15$ K

x_2	H^E (J·mol^{-1})	x_2	H^E (J·mol^{-1})	x_2	V^E (cm^3·mol^{-1})	x_2	V^E (cm^3·mol^{-1})
			1-Bromobutane (1) + 1-Butanol (2)				
0.0425	509	0.5011	955	0.0492	0.069	0.5795	0.120
0.0950	762	0.6021	829	0.0586	0.080	0.6017	0.113
0.1946	965	0.7039	658	0.0666	0.089	0.7052	0.080
0.2956	1038	0.8066	445	0.1028	0.118	0.7377	0.068
0.3487	1044	0.9068	217	0.1476	0.142	0.7795	0.043
0.3978	1031	0.9590	99	0.2212	0.157	0.7935	0.042
0.4498	995			0.2888	0.162	0.8398	0.026
				0.3571	0.160	0.8778	0.016
				0.4288	0.153	0.9016	0.010
				0.4771	0.143		
			1-Bromobutane (1) + 2-Methyl-2-propanol (2)				
0.0412	520	0.4931	1571	0.0479	0.171	0.5544	0.733
0.0923	916	0.5944	1497	0.0569	0.199	0.6457	0.692
0.1896	1272	0.6972	1328	0.1109	0.340	0.6965	0.646
0.2889	1469	0.8015	1040	0.1663	0.437	0.7644	0.572
0.3415	1533	0.9040	611	0.2269	0.531	0.7999	0.507
0.3902	1569	0.9578	321	0.2739	0.583	0.8558	0.411
0.4419	1576			0.3446	0.654	0.9293	0.239
				0.4204	0.710	0.9522	0.169
				0.4773	0.728		

Table 5. Coefficients C_j and Standard Deviations $\sigma(Q^E)$ for Least-Squares Representation by Eq 11 of H^E and V^E, at $T = 298.15$ K

mixture	Q^E	C_0	C_1	C_2	C_3	$\sigma(Q^E)$
x_1 1-bromobutane + x_2 1-butanol	H^E (J·mol^{-1})	22107	−62761	75057	−32338	10
	V^E (cm^3·mol^{-1})	2.799	−7.286	9.105	−4.631	0.003
x_1 1-bromobutane + x_2 2-methyl-2-propanol	H^E (J·mol^{-1})	18816	−33528	22249		15
	V^E (cm^3·mol^{-1})	5.025	−6.684	5.229		0.006

Table 6. Azeotropic Pressures and Mole Fractions

	1-bromobutane + 1-butanol				1-bromobutane + 2-methyl-2-propanol			
T (K)	z_2 exptl.	P_z (kPa) exptl.	z_2 calcd. eq 12	P_z (kPa) calcd. eq 14	z_2 exptl.	P_z (kPa) exptl.	z_2 calcd. eq 12	P_z (kPa) calcd. eq 14
278.15	0.013	1.860	0.014	1.876				
288.15	0.034	3.293	0.033	3.288				
293.15	0.044	4.295	0.043	4.290				
298.15	0.055	5.582	0.053	5.549	0.451	8.060	0.451	8.073
303.15	0.065	7.155	0.063	7.117	0.482	10.535	0.482	10.521
308.15	0.075	9.086	0.073	9.053	0.513	13.597	0.513	13.593
313.15	0.083	11.437	0.082	11.429	0.546	17.438	0.544	17.419
318.15					0.575	22.152	0.575	22.149
323.15	0.101	17.648	0.102	17.825	0.607	27.921	0.607	27.955

Table 7. Thermodynamic Excess Functions for 0.5 Alkanol + 0.5 Butanenitrile or 0.5 Butanone or 0.5 1-Bromobutane or 0.5 1-Chlorobutane or 0.5 Dipropyl Ether or 0.5 *n*-Hexane, at 298.15 K

	1-butanol			2-methyl-2-propanol		
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})
butanenitrile ($\mu = 4.1$ D)[a]	1588[b]	801[b]	0.105[b]	1851[c]	1158[c]	0.422[c]
butanone ($\mu = 3.4$ D)[a]	1325[d]	815[e]	0.010[d]	1571[d]	1203[f]	0.481[d]
1-bromobutane ($\mu = 2.2$ D)[a]	956[g]	−3[g]	0.141[g]	1560[g]	649[g]	0.728[g]
1-chlorobutane ($\mu = 2.1$ D)[a]	873[h]	−65[i]	0.061[h]	1548[h]	705[i]	0.675[h]
dipropyl ether ($\mu = 1.2$ D)[a]	743[d]	4[j]	−0.468[d]	965[d]	262[k]	0.314[d]
n-hexane	510[l]	−630[l]	0.08[l]	847[l]	−17[m]	0.921[n]

[a] McClelland.[28] [b] Garriga et al.[1] [c] Garriga et al.[3] [d] Iñarrea et al.[29] [e] Garriga et al.[5] [f] Garriga et al.[6] [g] This work. [h] Pérez et al.[30] [i] Garriga et al.[10] [j] Garriga et al.[8] [k] Garriga et al.[9] [l] Brown et al.[31] [m] Calculated from G^E data of Rodríguez el at.[32] [n] Pardo et al.,[33] at $T = 303.15$ K.

the branched isomer must be a more ordered liquid than the linear isomer.

On the other hand, by comparing the thermodynamic properties of mixtures of an alcohol with 1-chlorobutane or 1-bromobutane (approximately the same polarity), a similar behavior can be observed.

Nitrile and carbonyl groups are worse proton acceptors than ethers because the electrons around the oxygen ether have less s and more p character than those in ketones and nitriles.[34] In systems with an alcohol + a polar solvent containing oxygen or nitrogen atoms, the solvent polarity must not be the only parameter to interpret the excess properties since intermolecular hydrogen bonding between the hydroxyl group and oxygen or nitrogen atoms of solvent molecules must make an important contribution which will be larger with the ether group than with the nitrile or carbonyl group.

Even for binary systems, the interpretation of experimental results in terms of alcohol structure, specific interactions, and intermolecular hydrogen bonding is a very complicated question and more experimental results on adequately selected systems are necessary.

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