Vapor Liquid Equilibrium between (278.15 and 323.15) K and Excess Functions at $T = 298.15$ K for 1-Bromobutane with 2-Methyl-1-propanol or 2-Butanol

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Vapor pressures of (1-bromobutane + 2-methyl-1-propanol or 2-butanol) at 10 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 vapor pressure data to the Wilson equation 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 in industrial applications.[1] 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 1-chlorobutane + butanol isomers,[2,3] + ethanol, or + 1-hexanol[4] and 1-bromobutane + 1-butanol or + 2-methyl-2-propanol.[5] We report here vapor pressures at 10 temperatures for (1-bromobutane + 2-methyl-1-propanol) and for (1-bromobutane + 2-butanol). We have also measured excess enthalpies and excess volumes at $T = 298.15$ K.

Experimental Section

Chemicals. All of the chemicals were supplied by Aldrich. All of the chemicals had low water content, were stored over 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, 0.998 for 2-methyl-1-propanol, and 0.999 for 2-butanol.

Apparatus and Procedures. The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh,[6] except for some experimental details which have been described previously.[7,8] Each liquid was degassed by magnetic stirring under its own vapor pressure before mixing, with the vapor + air being pumped away periodically. The mixture cell containing a known mass of the first component was immersed in liquid nitrogen, and a known mass of the second component was added by gravity. The mixture cell, filled with 8−10 cm^3 of sample in each experiment, was connected to the manometric system, which was evacuated, and then the liquid sample was introduced by gravity into the vapor-pressure cell which is connected to one of the branches of the manometer. To prevent condensation effects on the mercury meniscus, the temperatures of the manometer and the connecting tube containing the vapor phase were maintained at 325.0 ± 0.1 K by circulating water from a thermostat. Uncertainties in the mole fractions are estimated to be less than 0.0003. The temperature of the liquid sample was controlled to within ±10 mK. Manometric levels were read with a cathetometer to within ±0.01 mm, and the pressure reproducibility was 10 Pa.

A calorimeter Thermometric 2277, 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).[9] 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 sample density is calculated from the vibration period with an uncertainty of ±0.000 02 g·cm^{-3}. The accuracy for V^E is estimated to be 0.002 cm^3·mol^{-1}.

Results

The molar volumes of the pure components used in the Barker analysis together with the experimental and calculated vapor pressures are presented in Table 1.

The second virial coefficient, at $T = 325.0$ K, of 1-bromobutane ($B_{11} = -1200$ cm^3 · mol^{-1}) was taken from Velasco et al.,[14] that of 2-methyl-1-propanol ($B_{22} = -3260$ cm^3·mol^{-1}) was calculated by interpolation of values taken from the TRC tables,[15] and that of 2-butanol ($B_{22} = -2640$ cm^3·mol^{-1}) was obtained by extrapolation from the Dymond and Smith[16] data compilation. The interaction virial coefficient was estimated with a cubic combination rule

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

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[17] to

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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			2-methyl-1-propanol			2-butanol		
T	V^0 [a]	P^0/kPa		V^0 [d]	P^0/kPa		V^0 [d]	P^0/kPa	
K	cm^3·mol^{-1}	b	c	cm^3·mol^{-1}	b	e	cm^3·mol^{-1}	b	e
278.15	105.6[f]	1.860	1.855	91.2	0.335	0.325	90.5	0.519	0.503
283.15	106.2[f]	2.480	2.477	91.6	0.505	0.488	90.9	0.780	0.755
288.15	106.8	3.265	3.269	92.0	0.739	0.719	91.4	1.137	1.110
293.15	107.4	4.261	4.264	92.5	1.057	1.044	91.9	1.648	1.606
298.15	108.0	5.506	5.502	92.9	1.501	1.491	92.4	2.324	2.284
303.15	108.7	7.039	7.027	93.4	2.133	2.099	92.8	3.256	3.198
308.15	109.3[f]	8.899	8.889	93.9	2.956	2.913	93.3	4.462	4.412
313.15	109.9[f]	11.148	11.143	94.3	4.026	3.988	93.9	6.048	6.003
318.15	110.5[f]	13.872	13.851	94.8	5.444	5.392	94.4	8.105	8.062
323.15	111.2[f]	17.092	17.077	95.3	7.237	7.203	94.9	10.706	10.691

[a] Timmermans.[10] [b] This work. [c] Riddick.[11] [d] TRC.[12] [e] Ambrose and Ghiassee.[13] [f] Interpolated values.

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) + 2-Methyl-1-propanol (2)						
					278.15 K						
0.0513	1.944	12	1.0170	7.9790	283	0.5834	1.731	−21	1.9392	1.2761	967
0.1003	1.967	30	1.0520	5.2368	490	0.6959	1.615	6	2.3753	1.1381	817
0.1992	1.933	11	1.1535	3.0600	780	0.7947	1.387	−8	2.9134	1.0614	617
0.3031	1.901	2	1.2968	2.1490	955	0.8393	1.280	25	3.2248	1.0376	507
0.3865	1.857	−16	1.4423	1.7543	1022	0.9219	0.877	−10	3.9645	1.0090	268
0.4782	1.817	−13	1.6417	1.4791	1031						
					283.15 K						
0.0513	2.606	13	1.0168	7.7530	284	0.5835	2.333	−25	1.9212	1.2657	964
0.1003	2.642	37	1.0515	5.1092	491	0.6959	2.172	8	2.3404	1.1323	812
0.1992	2.606	16	1.1520	2.9994	782	0.7948	1.883	7	2.8505	1.0585	612
0.3031	2.560	0	1.2935	2.1138	956	0.8394	1.689	−2	3.1421	1.0357	502
0.3865	2.513	−11	1.4367	1.7300	1022	0.9219	1.219	8	3.8255	1.0085	265
0.4783	2.440	−26	1.6321	1.4626	1030						
					288.15 K						
0.0512	3.440	14	1.0156	7.3638	280	0.5835	3.090	−36	1.8982	1.2613	964
0.1003	3.498	50	1.0486	4.9504	487	0.6960	2.888	16	2.3068	1.1300	812
0.1993	3.452	20	1.1458	2.9520	778	0.7949	2.513	15	2.8013	1.0574	613
0.3031	3.397	5	1.2841	2.0933	954	0.8394	2.246	−12	3.0829	1.0350	502
0.3866	3.326	−18	1.4243	1.7177	1021	0.9220	1.652	12	3.7398	1.0083	265
0.4783	3.232	−36	1.6156	1.4550	1029						
					293.15 K						
0.0512	4.496	22	1.0139	6.8865	273	0.5836	4.060	−43	1.8721	1.2615	967
0.1003	4.576	64	1.0444	4.7698	477	0.6961	3.802	23	2.2746	1.1303	816
0.1993	4.514	19	1.1368	2.9128	769	0.7949	3.318	14	2.7631	1.0576	616
0.3031	4.437	−6	1.2705	2.0831	949	0.8395	2.989	−11	3.0417	1.0351	506
0.3866	4.360	−22	1.4072	1.7142	1018	0.9220	2.221	11	3.6930	1.0083	267
0.4784	4.246	−36	1.5944	1.4542	1030						
					298.15 K						
0.0512	5.818	27	1.0127	6.4746	267	0.5837	5.285	−52	1.8453	1.2578	964
0.1003	5.933	80	1.0412	4.5885	469	0.6962	4.938	13	2.2372	1.1284	815
0.1993	5.872	31	1.1296	2.8590	761	0.7950	4.337	14	2.7114	1.0568	616
0.3032	5.774	0	1.2591	2.0616	942	0.8396	3.921	−18	2.9812	1.0346	505
0.3867	5.666	−28	1.3921	1.7023	1013	0.9221	2.981	36	3.6098	1.0082	267
0.4784	5.521	−46	1.5746	1.4475	1026						
					303.15 K						
0.0511	7.461	32	1.0117	6.0998	261	0.5838	6.823	−65	1.8169	1.2503	955
0.1003	7.629	101	1.0388	4.4016	461	0.6964	6.385	19	2.1935	1.1245	807
0.1993	7.554	26	1.1237	2.7908	751	0.7952	5.625	17	2.6453	1.0549	609
0.3032	7.459	11	1.2491	2.0290	931	0.8397	5.113	−15	2.9005	1.0334	500
0.3867	7.311	−35	1.3782	1.6821	1003	0.9222	3.934	38	3.4903	1.0079	263
0.4785	7.118	−64	1.5552	1.4349	1016						
					308.15 K						
0.0510	9.470	36	1.0114	5.8643	259	0.5840	8.721	−78	1.7948	1.2399	945
0.1002	9.685	100	1.0378	4.2615	458	0.6965	8.177	44	2.1544	1.1187	797
0.1993	9.627	20	1.1210	2.7248	746	0.7953	7.225	45	2.5797	1.0521	600
0.3033	9.507	−6	1.2439	1.9918	925	0.8398	6.498	−84	2.8170	1.0316	492
0.3868	9.346	−40	1.3700	1.6569	995	0.9222	5.150	78	3.3589	1.0074	259
0.4786	9.133	−44	1.5422	1.4180	1007						
					313.15 K						
0.0509	11.899	52	1.0105	5.5713	253	0.5841	11.055	−103	1.7735	1.2385	946
0.1002	12.204	136	1.0353	4.1241	451	0.6968	10.383	37	2.1270	1.1181	798
0.1993	12.148	18	1.1149	2.6848	739	0.7955	9.206	21	2.5451	1.0519	602
0.3033	12.015	−11	1.2341	1.9776	920	0.8400	8.423	−32	2.7785	1.0315	494
0.3869	11.814	−59	1.3572	1.6501	992	0.9224	6.681	69	3.3114	1.0074	260
0.4788	11.576	−41	1.5257	1.4148	1006						

Table 2 (Continued)

1-Bromobutane (1) + 2-Methyl-1-propanol (2)											
318.15 K											
0.0508	14.784	13	1.0097	5.2649	247	0.5844	13.891	−132	1.7464	1.2311	934
0.1001	15.225	140	1.0332	3.9567	442	0.6971	13.072	48	2.0856	1.1142	788
0.1992	15.204	0	1.1096	2.6186	728	0.7958	11.619	12	2.4834	1.0500	594
0.3034	15.177	87	1.2249	1.9452	908	0.8402	10.691	−33	2.7038	1.0303	487
0.3870	14.824	−80	1.3441	1.6298	980	0.9225	8.595	86	3.2035	1.0071	256
0.4790	14.536	−54	1.5072	1.4021	994						
323.15 K											
0.0506	18.240	48	1.0086	4.9010	238	0.5847	17.311	−131	1.7160	1.2288	926
0.1001	18.809	187	1.0302	3.7711	429	0.6975	16.280	28	2.0462	1.1133	783
0.1992	18.876	49	1.1016	2.5589	711	0.7961	14.613	47	2.4336	1.0497	591
0.3034	18.708	−3	1.2115	1.9229	892	0.8405	13.484	−33	2.6483	1.0301	484
0.3872	18.441	−51	1.3262	1.6189	966	0.9227	10.975	94	3.1356	1.0070	255
0.4792	18.003	−115	1.4839	1.3969	983						
1-Bromobutane (1) + 2-Butanol (2)											
278.15 K											
0.0953	2.068	22	1.0512	5.6042	484	0.4889	1.953	−20	1.6858	1.4580	1044
0.0976	2.066	20	1.0532	5.5058	493	0.4926	1.948	−23	1.6953	1.4495	1042
0.1500	2.061	9	1.1040	3.9298	669	0.6049	1.868	−19	2.0356	1.2466	958
0.2111	2.056	8	1.1755	2.9493	823	0.7247	1.703	−21	2.5479	1.1131	775
0.3087	2.048	14	1.3164	2.1297	979	0.7997	1.540	−13	2.9885	1.0590	613
0.3852	2.020	5	1.4531	1.7669	1038	0.9024	1.217	47	3.8303	1.0141	332
283.15 K											
0.0952	2.788	21	1.0522	5.4502	489	0.4889	2.657	−15	1.6766	1.4317	1035
0.0976	2.774	7	1.0542	5.3534	497	0.4927	2.641	−28	1.6859	1.4235	1033
0.1500	2.782	5	1.1053	3.8148	673	0.6050	2.529	−23	2.0112	1.2307	945
0.2111	2.781	6	1.1767	2.8646	825	0.7247	2.314	−11	2.4905	1.1048	761
0.3087	2.772	14	1.3162	2.0749	978	0.7997	2.100	5	2.8931	1.0543	601
0.3852	2.742	11	1.4505	1.7268	1034	0.9024	1.620	26	3.6402	1.0128	324
288.15 K											
0.0952	3.700	33	1.0485	5.2360	480	0.4889	3.533	−22	1.6552	1.4222	1029
0.0975	3.668	0	1.0504	5.1470	489	0.4927	3.526	−25	1.6643	1.4141	1028
0.1500	3.698	11	1.0994	3.7157	664	0.6051	3.372	−27	1.9801	1.2253	941
0.2111	3.690	3	1.1684	2.8118	817	0.7248	3.093	−11	2.4425	1.1021	758
0.3087	3.674	9	1.3042	2.0493	970	0.7998	2.813	5	2.8282	1.0528	597
0.3852	3.645	13	1.4351	1.7105	1027	0.9025	2.196	30	3.5379	1.0124	322
293.15 K											
0.0952	4.838	24	1.0450	4.9851	470	0.4889	4.668	−21	1.6305	1.4076	1016
0.0975	4.824	7	1.0468	4.9040	479	0.4928	4.649	−35	1.6395	1.3996	1015
0.1499	4.846	−5	1.0935	3.5893	652	0.6051	4.454	−31	1.9424	1.2170	929
0.2111	4.858	2	1.1600	2.7399	804	0.7249	4.092	−14	2.3816	1.0980	747
0.3087	4.850	19	1.2914	2.0124	957	0.7998	3.733	6	2.7438	1.0506	589
0.3853	4.825	36	1.4182	1.6861	1014	0.9025	2.953	35	3.4013	1.0118	317
298.15 K											
0.0951	6.271	21	1.0417	4.7712	460	0.4889	6.098	−23	1.6082	1.3982	1008
0.0975	6.274	19	1.0434	4.6971	469	0.4928	6.070	−45	1.6170	1.3903	1007
0.1499	6.305	−8	1.0879	3.4857	642	0.6052	5.826	−37	1.9103	1.2118	922
0.2111	6.325	−2	1.1519	2.6842	793	0.7250	5.368	−16	2.3333	1.0954	741
0.3087	6.330	30	1.2791	1.9859	947	0.7999	4.910	4	2.6798	1.0492	584
0.3853	6.285	37	1.4022	1.6695	1005	0.9026	3.941	46	3.3040	1.0115	314
303.15 K											
0.0950	8.061	17	1.0394	4.5667	452	0.4889	7.921	−5	1.5875	1.3833	995
0.0974	8.053	2	1.0411	4.4977	461	0.4929	7.879	−38	1.5962	1.3755	994
0.1499	8.123	−20	1.0839	3.3727	632	0.6053	7.553	−46	1.8775	1.2033	909
0.2111	8.161	−12	1.1458	2.6161	782	0.7252	6.969	−25	2.2788	1.0912	730
0.3087	8.186	38	1.2692	1.9491	935	0.8000	6.415	17	2.6035	1.0469	575
0.3854	8.141	57	1.3886	1.6448	992	0.9027	5.188	34	3.1807	1.0109	308
308.15 K											
0.0949	10.230	13	1.0362	4.3834	442	0.4890	10.139	−14	1.5663	1.3793	990
0.0973	10.212	−15	1.0378	4.3201	451	0.4930	10.111	−32	1.5750	1.3715	989
0.1498	10.339	−34	1.0781	3.2879	621	0.6055	9.735	−24	1.8497	1.2014	906
0.2110	10.414	−16	1.1374	2.5746	771	0.7254	8.989	−35	2.2418	1.0904	729
0.3087	10.467	53	1.2566	1.9329	926	0.8002	8.290	−8	2.5588	1.0465	574
0.3854	10.427	85	1.3726	1.6361	985	0.9028	6.827	49	3.1215	1.0108	308
313.15 K											
0.0947	12.851	−9	1.0337	4.1965	432	0.4890	12.883	−3	1.5455	1.3688	979
0.0972	12.847	−29	1.0353	4.1378	441	0.4931	12.843	−30	1.5540	1.3610	977
0.1497	13.055	−37	1.0737	3.1871	609	0.6057	12.382	−25	1.8190	1.1956	896
0.2109	13.174	−14	1.1306	2.5165	759	0.7256	11.432	−80	2.1949	1.0876	720
0.3087	13.264	75	1.2459	1.9038	913	0.8004	10.623	−10	2.4965	1.0449	567
0.3855	13.228	119	1.3582	1.6175	972	0.9029	8.877	72	3.0274	1.0104	304

Table 2 (Continued)

1-Bromobutane (1) + 2-Butanol (2)												
318.15 K												
0.0948	16.045	−14	1.0314	3.9979	422	0.4889	16.273	39	1.5232	1.3584	965	
0.0973	16.048	−33	1.0329	3.9450	430	0.4929	16.183	−38	1.5310	1.3512	964	
0.1497	16.356	−38	1.0692	3.0800	596	0.6055	15.556	−108	1.7857	1.1903	884	
0.2110	16.531	−15	1.1236	2.4556	745	0.7259	14.531	−56	2.1468	1.0849	710	
0.3087	16.663	84	1.2343	1.8745	898	0.8006	13.526	−8	2.4334	1.0435	559	
0.3853	16.641	146	1.3425	1.5994	958	0.9031	11.430	74	2.9342	1.0100	300	
323.15 K												
0.0945	19.857	1	1.0289	3.8325	411	0.4890	20.302	13	1.5026	1.3527	956	
0.0971	19.836	−52	1.0303	3.7834	420	0.4930	20.246	−26	1.5104	1.3455	955	
0.1496	20.257	−77	1.0646	2.9933	584	0.6057	19.593	−33	1.7578	1.1875	877	
0.2108	20.520	−50	1.1164	2.4088	731	0.7255	18.288	−79	2.1064	1.0840	707	
0.3086	20.760	102	1.2228	1.8540	886	0.8009	17.064	−51	2.3867	1.0428	555	
0.3854	20.777	197	1.3275	1.5876	946	0.9033	14.621	80	2.8710	1.0099	298	

Table 3. Wilson Parameters and Standard Deviations, $\sigma(P)$, of eq 9

	1-bromobutane (1) + 2-methyl-1-propanol (2)			1-bromobutane (1) + 2-butanol (2)		
T/K	Λ_{12}	Λ_{21}	σ/Pa	Λ_{12}	Λ_{21}	σ/Pa
278.15	0.4956	0.1030	17	0.4918	0.0913	22
283.15	0.5193	0.1046	18	0.5329	0.0875	17
288.15	0.5280	0.1152	26	0.5459	0.0996	20
293.15	0.5244	0.1333	31	0.5673	0.1124	24
298.15	0.5302	0.1485	39	0.5799	0.1264	29
303.15	0.5455	0.1613	49	0.6034	0.1364	32
308.15	0.5707	0.1661	62	0.6053	0.1537	40
313.15	0.5701	0.1817	67	0.6201	0.1675	57
318.15	0.5857	0.1951	81	0.6341	0.1834	70
323.15	0.5845	0.2193	93	0.6380	0.2018	84

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

x_2	H^E / $J \cdot mol^{-1}$	x_2	H^E / $J \cdot mol^{-1}$	x_2	V^E / $cm^3 \cdot mol^{-1}$	x_2	V^E / $cm^3 \cdot mol^{-1}$
1-Bromobutane (1) + 2-Methyl-1-propanol (2)							
0.0421	530	0.4990	1207	0.0576	0.077	0.5655	0.186
0.0942	851	0.6000	1081	0.1063	0.124	0.6332	0.157
0.1932	1125	0.7021	891	0.1475	0.146	0.6772	0.126
0.2938	1248	0.8052	636	0.2348	0.190	0.7160	0.102
0.3468	1271	0.9060	330	0.2586	0.198	0.8210	0.051
0.3957	1272	0.9587	159	0.3910	0.221	0.8385	0.044
0.4476	1245			0.4368	0.219	0.8690	0.025
				0.5451	0.198	0.9469	0.007
1-Bromobutane (1) + 2-Butanol (2)							
0.0424	520	0.5006	1508	0.0408	0.151	0.5140	0.449
0.0948	924	0.6015	1395	0.0848	0.223	0.5484	0.440
0.1942	1282	0.7035	1191	0.1407	0.293	0.6292	0.397
0.2951	1465	0.8062	887	0.2281	0.374	0.6450	0.382
0.3482	1519	0.9066	489	0.2864	0.408	0.7188	0.325
0.3973	1542	0.9590	246	0.3642	0.440	0.7739	0.260
0.4492	1532			0.3923	0.448	0.8388	0.186
				0.4098	0.451	0.8639	0.150
				0.4148	0.448	0.9284	0.076

the Wilson[18] correlation. The activity coefficients are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{2}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{3}$$

with

$$\Lambda_{ij} = \frac{V_j^0}{V_i^0}\exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{4}$$

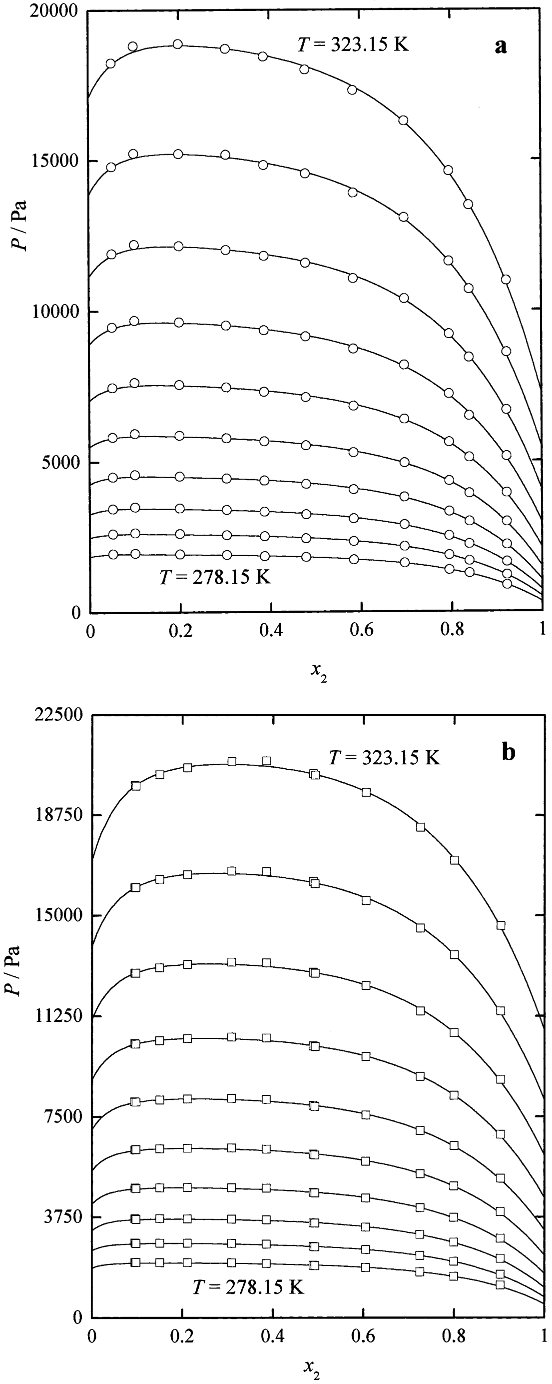

Figure 1. Vapor pressures plotted against liquid-phase composition of alcohol, at 10 temperatures between 278.15 and 323.15 K: (a) {x_1 1-bromobutane + x_2 2-methyl-1-propanol} and (b) {x_1 1-bromobutane + x_2 2-butanol}.

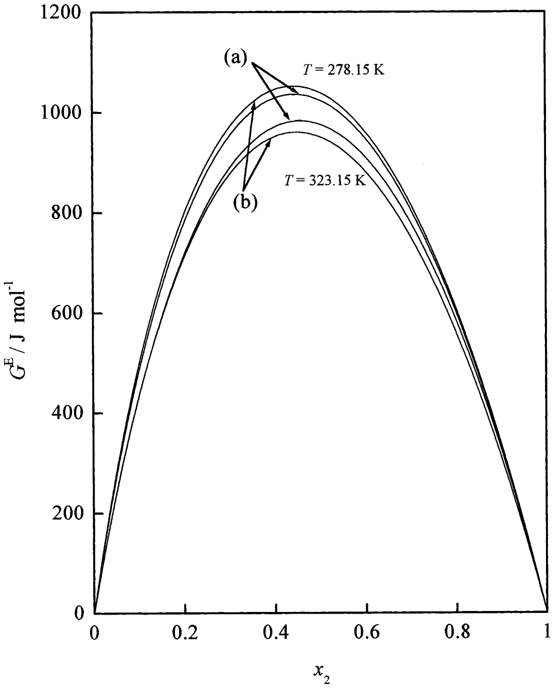

Figure 2. Excess molar Gibbs energies G^E at 278.15 K and 323.15 K: (a) $\{x_1$ 1-bromobutane + x_2 2-methyl-1-propanol$\}$ and (b) $\{x_1$ 1-bromobutane + x_2 2-butanol$\}$, plotted as a function of mole fraction of alcohol.

where the subscripts 1 and 2 stand for 1-bromobutane and alcohol, respectively. V^0 is the molar volume, and λ's are negative interaction constants between the molecules designated in the subscripts. The vapor pressure is then given by

$$P_{calc} = x_1 \gamma_1 P_1^0 R_1 + x_2 \gamma_2 P_2^0 R_2 \tag{5}$$

where the nonideality of the vapor phase is taken into account with the corrections

$$R_1 = \exp\{[(V_1^0 - B_{11})(P - P_1^0) - P\,\delta_{12} y_2^{\,2}]/RT\} \tag{6}$$

$$R_2 = \exp\{[(V_2^0 - B_{22})(P - P_2^0) - P\,\delta_{12} y_1^{\,2}]/RT\} \tag{7}$$

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

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{8}$$

For a given composition in Table 2, when the sample temperature is changed, a slight variation of the true liquid mole fraction is observed, because of an enrichment of the most volatile component in the vapor phase. In Table 3, the Wilson parameters Λ_{12} and Λ_{21} are collected, together with the standard deviations defined by

$$\sigma(P) = \{\sum_{i=1}^{N} (\Delta P)_i^{\,2}/(N-2)\}^{1/2} \tag{9}$$

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, parts a and b. For both systems, Figure 2 shows the analytical equations for G^E at the lowest and highest temperatures. A negative temperature coefficient was observed in both cases.

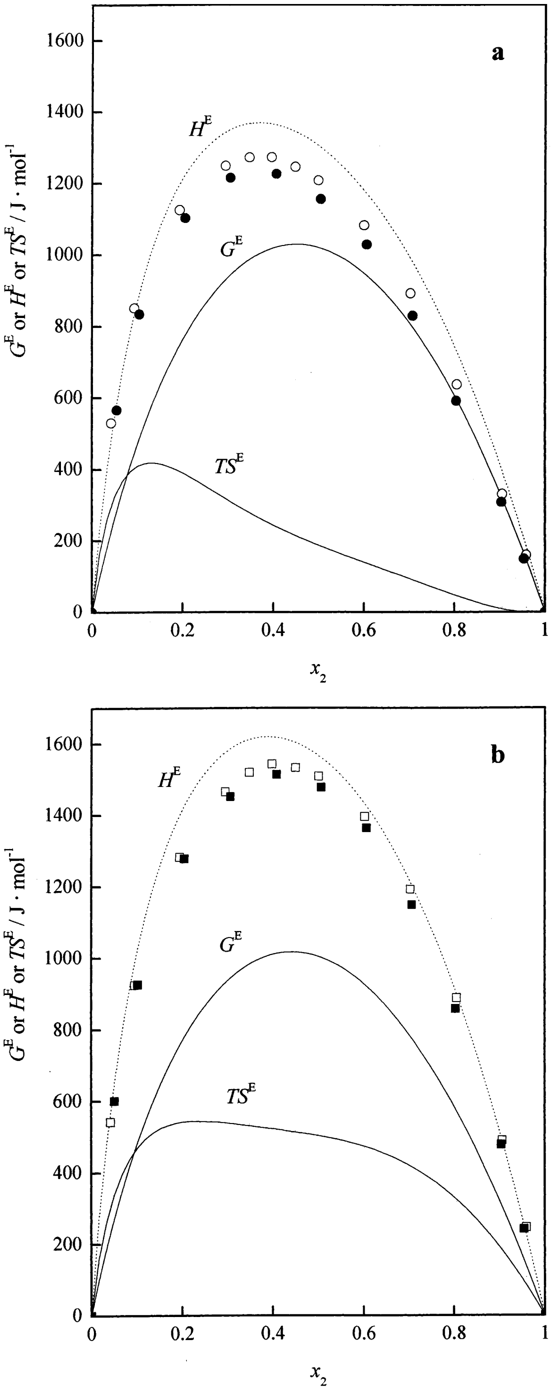

Figure 3. Thermal excess molar functions at T = 298.15 K: (a) $\{x_1$ 1-bromobutane + x_2 2-methyl-1-propanol$\}$; ○, experimental H^E; (b) $\{x_1$ 1-bromobutane + x_2 2-butanol$\}$; □, experimental H^E; ● and ■, Artigas et al.;[19] ···, Gibbs–Helmholtz H^E; and –, G^E and TS^E.

Experimental excess molar enthalpies and volumes, at 298.15 K, are given in Table 4 and plotted in Figures 3 and 4. The results were fitted with a polynomial

$$Q^E = x_1 x_2 \sum_{j=0}^{m} C_j x_2^{j/2} \tag{10}$$

where Q^E denotes H^E or V^E and x_1 and x_2 denote the mole fractions of 1-bromobutane and alcohol, respectively. For alcoholic mixtures, this polynomial[21,22] represents the experimental behavior better than the classical Redlich–

Table 5. Coefficients C_j and Standard Deviations $\sigma(Q^E)$ for Least-Squares Representation by eq 10 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 2-methyl-1-propanol	$H^E/(J\cdot mol^{-1})$	22057	−56464	63289	−25312	9
	$V^E/(cm^3\cdot mol^{-1})$	2.542	−6.793	11.045	−6.880	0.003
x_1 1-bromobutane + x_2 2-butanol	$H^E/(J\cdot mol^{-1})$	21005	−46452	46733	−15552	10
	$V^E/(cm^3\cdot mol^{-1})$	6.863	−21.131	30.807	−15.603	0.003

Table 6. Azeotropic Presures and Mole Fractions

	1-bromobutane + 2-methyl-1-propanol				1-bromobutane + 2-butanol			
	z_2	P_z/kPa	z_2	P_z/kPa	z_2	P_z/kPa	z_2	P_z/kPa
T/K	exptl.	exptl.	calcd. eq 11	calcd. eq 13	exptl.	exptl.	calcd. eq 11	calcd. eq 13
278.15	0.0869	1.937	0.0850	1.952	0.1488	2.052	0.1452	2.072
283.15	0.0990	2.606	0.0969	2.605	0.1631	2.778	0.1611	2.776
288.15	0.1092	3.449	0.1089	3.442	0.1776	3.689	0.1771	3.683
293.15	0.1187	4.514	0.1208	4.504	0.1930	4.857	0.1930	4.837
298.15	0.1293	5.859	0.1328	5.841	0.2076	6.327	0.2090	6.297
303.15	0.1425	7.545	0.1447	7.510	0.2232	8.173	0.2249	8.125
308.15	0.1549	9.620	0.1567	9.578	0.2407	10.435	0.2409	10.398
313.15	0.1687	12.138	0.1686	12.121	0.2573	13.205	0.2568	13.203
318.15	0.1816	15.207	0.1806	15.225	0.2743	16.587	0.2728	16.638
323.15	0.1951	18.827	0.1925	18.990	0.2931	20.659	0.2887	20.818

Table 7. Thermodynamic Excess Functions for 0.5 Butanol Isomer + 0.5 Butanenitrile, or 0.5 Butanone, or 0.5 1-Bromobutane, or 0. 5 1-Chlorobutane, or 0.5 *n*-Hexane, at 298.15 K

butanol isomer	excess functions	butanenitrile (μ = 4.1 D)[a]	butanone (μ = 3.4 D)[a]	1-bromobutane (μ = 2.2 D)[a]	1-chlorobutane (μ = 2.1 D)[a]	*n*-hexane
1-butanol	$H^E/(J\cdot mol^{-1})$	1588[b]	1325[c]	956[d]	873[e]	510[f]
	$TS^E/(J\cdot mol^{-1})$	801[b]	815[g]	−3[d]	−65[h]	−630[f]
	$V^E/(cm^3\cdot mol^{-1})$	0.105[b]	0.010[c]	0.141[d]	0.061[e]	0.08[f]
2-methyl-1-propanol	$H^E/(J\cdot mol^{-1})$	1810[i]	1488[j]	1206[k]	1124[l]	658[f]
	$TS^E/(J\cdot mol^{-1})$	1017[i]	1036[j]	187[k]	179[l]	−488[m]
	$V^E/(cm^3\cdot mol^{-1})$	0.137[n]	0.091[j]	0.207[k]	0.144[l]	0.184[o]
2-butanol	$H^E/(J\cdot mol^{-1})$	1985[p]	1630[q]	1507[k]	1415[l]	858[f]
	$TS^E/(J\cdot mol^{-1})$	1223[p]	1174[q]	503[k]	513[l]	−213[m]
	$V^E/(cm^3\cdot mol^{-1})$	0.349[n]	0.352[q]	0.452[k]	0.398[l]	0.439[r]
2-methyl-2-propanol	$H^E/(J\cdot mol^{-1})$	1851[i]	1571[c]	1560[d]	1548[e]	847[f]
	$TS^E/(J\cdot mol^{-1})$	1158[i]	1203[j]	649[d]	705[h]	−17[m]
	$V^E/(cm^3\cdot mol^{-1})$	0.422[i]	0.481[c]	0.728[d]	0.675[e]	0.921[r]

[a] McClelland.[24] [b] Garriga et al.[25] [c] Iñarrea et al.[26] [d] Garriga et al.[5] [e] Pérez et al.[27] [f] Brown et al.[28] [g] Garriga et al.[29] [h] Garriga et al.[2] [i] Garriga et al.[30] [j] Garriga et al.[31] [k] This work. [l] Garriga et al.[3] [m] Calculated from G^E data from Rodríguez et al.[32] [n] Martínez et al.[33] [o] Berro et al.[34] [p] Garriga et al.[35] [q] Garriga et al.[36] [r] Pardo et al.,[37] at T = 303.15 K.

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 $\partial\Lambda_{ij}/\partial T$ have been obtained by fitting the Wilson parameters as a linear function of the temperature. The H^E-calculated values, 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 considerably 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 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 temperature according to the equation

$$z_2 = a + b(T/\text{K}) \tag{11}$$

For 1-bromobutane + 2-mehtyl-1-propanol, $a = -0.5798$ and $b = 2.390 \times 10^{-3}\ \text{K}^{-1}$, and for 1-bromobutane + 2-butanol, $a = -0.7421$ and $b = 3.190 \times 10^{-3}\ \text{K}^{-1}$.

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

$$\text{d} \ln P_z/\text{d}T = \Delta_{\text{vap}}H_z/RT^2 \tag{12}$$

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

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

For 1-bromobutane + 2-mehtyl-1-propanol, $A = 23.91$ and $B = -\ 4544$ K, and for 1-bromobutane + 2-butanol, $A = 24.20$ and $B = -\ 4608$ K. Experimental and calculated (from eqs 11 and 13) 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, solvent−solvent and OH-group−solvent interactions come into play, and the excess molar entropies and enthalpies are much more positive than those with *n*-hexane in place of the polar

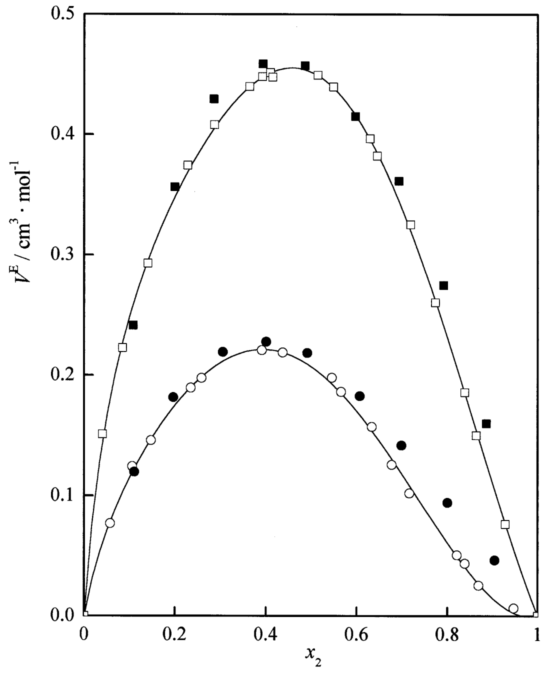

Figure 4. Excess molar volumes at T = 298.15 K: ○, {x_1 1-bromobutane + x_2 2-methyl-1-propanol}; □, {x_1 1-bromobutane + x_2 2-butanol}; ● and ■, Artigas et al.[20]

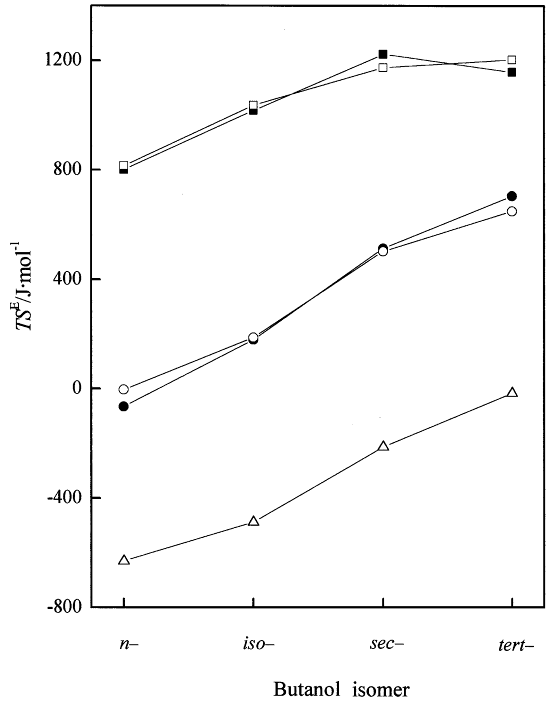

Figure 5. Excess molar entropies, at T = 298.15 K, for mixtures {0.5 butanol isomer + 0.5 solvent} with solvent: ○, 1-bromobutane; ●, 1-chlorobutane; □, butanone; ■, butanenitrile; △, n-hexane.

solvent, as shown in Figure 5 and Table 7. By increasing the solvent polarity, both properties increase as more hydrogen bonds are broken at a given mole fraction because of the stronger hydroxyl group-solvent interaction.

With the same solvent, all excess functions increase on going from 1-butanol to 2-methyl-2-propanol, which suggests an increase of the liquid butanol structure with the branching and shielding of the OH group.

For these systems, a theoretical analysis of the volumetric behavior is a very complicated question, as V^E is the resultant of structural and interaction effects that are not easy to evaluate.

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