Vapor Liquid Equilibrium between (278.15 and 323.15) K and Excess Functions at $T = 298.15$ K for 1-Bromobutane with 1-Octanol or 1-Decanol

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Vapor pressures of (1-bromobutane + 1-octanol or 1-decanol) at several temperatures between (278.15 and 323.15 K) were measured by a static method. 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. Excess molar enthalpies H^E and volumes V^E of (1-bromobutane + 1-octanol) were also measured at 298.15 K. V^E at 298.15 K was compared with predictions of the ERAS model.

Introduction

Hydrogen bonding plays an important role both in 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. Thermodynamic data of 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. Following our studies on thermodynamic properties of binary systems of (alcohol + 1-chlorobutane)[2−5] or (alcohol + 1-bromobutane),[6−8] we report vapor pressures at several temperatures for (1-bromobutane + 1-octanol) and for (1-bromobutane + 1-decanol). Excess enthalpies and excess volumes for (1-bromobutane + 1-octanol) have been measured at $T = 298.15$ K. A description of the excess volume according to the ERAS model is presented. Isothermal vapor pressure data were not found for these systems in the literature.

Experimental Section

Chemicals. All the chemicals were supplied by Aldrich. 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, 0.995 for 1-octanol, and 0.986 for 1-decanol.

Apparatus and Procedures. The vapor pressure measurements were performed by a static method. The apparatus is similar to that of Marsh,[9] except for some experimental details which have been described previously.[10,11] Each liquid was degassed by magnetic stirring under its own vapor pressure before mixing, with periodic vacuum pumping of the vapor + air. 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 to 10) cm^3 of sample in each experiment, was connected to a 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 temperature of the manometer and the connecting tube containing the vapor phase was 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 pressure reproducibility was 10 Pa.

A Thermometric 2277 calorimeter, together with two Shimadzu (model LC-10AD) variable speed piston pumps, was 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).[12] The experimental results agreed with the literature data with an accuracy of 20 J·mol^{-1}, 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 operates 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.,[17] and those of 1-octanol ($B_{22} = -19\,850$ cm^3·mol^{-1}) and 1-decanol ($B_{22} = -40\,560$ cm^3·mol^{-1}) were calculated from the Tsonopoulos[18] correlation. The interaction virial coefficient was estimated with a cubic combination rule,

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

Table 2 presents our vapor pressure measurements together with the activity coefficients γ_1 and γ_2 of 1-bro-

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

	1-bromobutane			1-octanol			1-decanol		
T	$V^{\circ\, a}$	P°/kPa		$V^{\circ\, d}$	P°/kPa		$V^{\circ\, d}$	P°/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	110.5	<0.003	<0.003			
283.15	106.2^f	2.480	2.477	111.0	<0.003	<0.003	189.3	<0.003	<0.003
288.15	106.8	3.265	3.269	111.5	<0.003	<0.003	190.0	<0.003	<0.003
293.15	107.4	4.261	4.264	112.1	0.003	0.003	190.7	<0.003	<0.003
298.15	108.0	5.506	5.502	112.6	0.007	0.006	191.5	<0.003	<0.003
303.15	108.7	7.039	7.027	113.1	0.011	0.011	192.3	<0.003	<0.003
308.15	109.3^f	8.899	8.889	113.6	0.019	0.019	193.1	<0.003	<0.003
313.15	109.9^f	11.148	11.143	114.2	0.031	0.031	193.9	0.004	0.004
318.15	110.5^f	13.872	13.851	114.7	0.051	0.050	194.7	0.007	0.006
323.15	111.2^f	17.092	17.077	115.3	0.080	0.079	195.6	0.011	0.011

[a] Timmermans.[13] [b] This work. [c] Riddick.[14] [d] TRC.[15] [e] TRC.[16] [f] Interpolated values.

mobutane and alcohol, respectively, and the excess molar Gibbs energy G^E values fitted by Barker's method[19] to the Wilson correlation[20]

$$G^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (2)$$

The activity coefficient of component i is given by

$$\ln \gamma_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j\left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j}\right] \quad (3)$$

with

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

where the subscripts 1 and 2 stand for 1-bromobutane and alcohol, respectively. V_i° is the molar volume of the pure component i, and λ_{ij} is the interaction constant between the molecules i and j. The vapor pressure is then given by

$$P_{\text{calc}} = x_1\gamma_1 P_1^\circ R_1 + x_2\gamma_2 P_2^\circ R_2 \quad (5)$$

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

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

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

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

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (8)$$

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

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

ΔP values are the residual pressures according to Barker's method, and N is the number of experimental points. To obtain a good fit by means of a Redlich−Kister polynomial, at least four parameters are necessary. Vapor pressure−liquid composition curves are shown in parts a and b of Figure 1. 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.

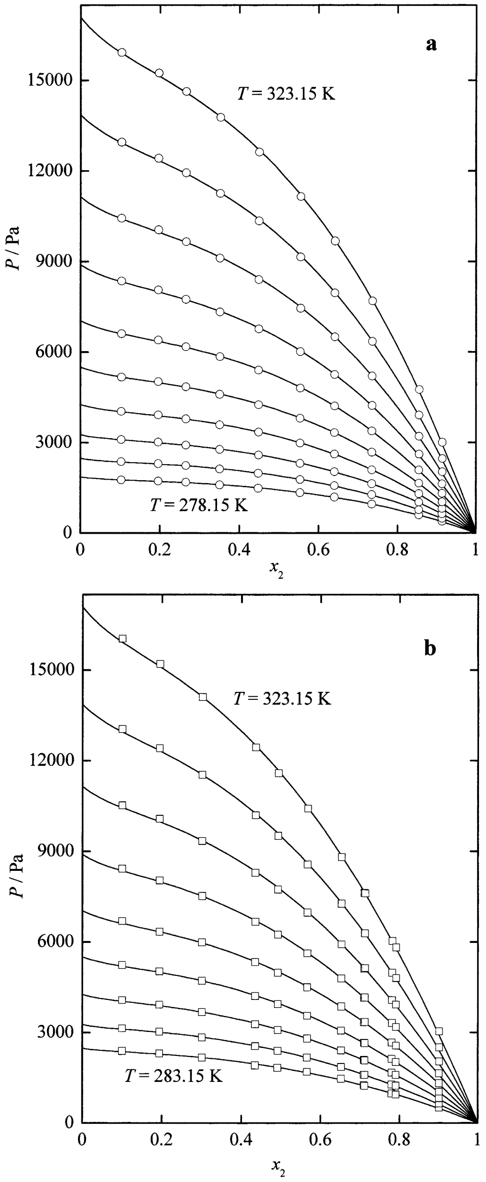

Figure 1. Vapor pressures plotted against liquid-phase composition of alcohol, at working temperatures: (a) {(x_1)1-bromobutane + (x_2)1-octanol}; (b) {(x_1)1-bromobutane + (x_2)1-decanol}.

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-Octanol (2)											
T = 278.15 K											
0.1029	1.763	−3	1.0584	3.5858	422	0.5528	1.339	−12	1.6240	1.1586	690
0.1957	1.728	12	1.1473	2.2322	619	0.6397	1.191	3	1.7723	1.0918	607
0.2650	1.687	13	1.2241	1.7942	702	0.7345	0.964	1	1.9507	1.0449	485
0.3503	1.600	−6	1.3290	1.4886	750	0.8543	0.603	6	2.2038	1.0121	290
0.4477	1.491	−12	1.4625	1.2874	747	0.9136	0.384	8	2.3418	1.0041	179
T = 283.15 K											
0.1029	2.374	16	1.0602	3.5033	427	0.5529	1.779	−7	1.6108	1.1488	682
0.1957	2.301	9	1.1493	2.1789	622	0.6398	1.569	6	1.7502	1.0857	599
0.2650	2.236	3	1.2252	1.7561	703	0.7345	1.272	12	1.9158	1.0417	477
0.3504	2.125	−14	1.3279	1.4629	748	0.8543	0.769	−6	2.1467	1.0112	284
0.4477	1.984	−11	1.4569	1.2709	742	0.9136	0.489	3	2.2708	1.0038	175
T = 288.15 K											
0.1030	3.101	9	1.0557	3.4104	419	0.5530	2.310	−14	1.5930	1.1475	681
0.1958	3.018	21	1.1415	2.1558	615	0.6399	2.038	5	1.7297	1.0850	598
0.2651	2.920	3	1.2153	1.7451	697	0.7346	1.639	−1	1.8921	1.0414	477
0.3504	2.777	−13	1.3157	1.4577	743	0.8544	1.021	14	2.1184	1.0111	285
0.4478	2.592	−8	1.4420	1.2683	739	0.9137	0.636	4	2.2400	1.0037	175
T = 293.15 K											
0.1030	4.034	10	1.0528	3.3050	413	0.5531	2.984	−13	1.5736	1.1431	674
0.1958	3.916	24	1.1357	2.1179	608	0.6400	2.620	4	1.7052	1.0824	592
0.2651	3.786	5	1.2075	1.7228	689	0.7347	2.100	−3	1.8607	1.0401	472
0.3505	3.593	−19	1.3050	1.4445	736	0.8544	1.303	14	2.0762	1.0107	281
0.4479	3.352	−7	1.4276	1.2606	732	0.9137	0.815	8	2.1913	1.0036	173
T = 298.15 K											
0.1030	5.173	−4	1.0479	3.1902	400	0.5532	3.809	−10	1.5520	1.1419	669
0.1959	5.025	35	1.1266	2.0884	595	0.6401	3.337	6	1.6807	1.0818	588
0.2652	4.854	15	1.1956	1.7094	678	0.7349	2.681	4	1.8329	1.0398	469
0.3506	4.598	−16	1.2902	1.4385	726	0.8545	1.656	16	2.0439	1.0107	280
0.4481	4.258	−27	1.4096	1.2579	725	0.9138	1.029	1	2.1566	1.0036	172
T = 303.15 K											
0.1031	6.607	0	1.0461	3.1182	397	0.5534	4.808	−32	1.5389	1.1389	667
0.1960	6.403	46	1.1228	2.0614	592	0.6403	4.218	3	1.6642	1.0800	586
0.2653	6.179	20	1.1904	1.6936	675	0.7350	3.385	3	1.8118	1.0389	468
0.3508	5.852	−14	1.2830	1.4292	724	0.8547	2.092	25	2.0158	1.0104	279
0.4482	5.410	−29	1.3998	1.2525	722	0.9138	1.315	20	2.1243	1.0035	172
T = 308.15 K											
0.1031	8.355	24	1.0434	3.0279	390	0.5537	6.016	−34	1.5222	1.1364	662
0.1961	8.062	65	1.1172	2.0314	584	0.6406	5.257	−6	1.6441	1.0786	582
0.2654	7.751	15	1.1827	1.6774	668	0.7352	4.228	11	1.7876	1.0382	465
0.3510	7.333	−23	1.2729	1.4205	717	0.8548	2.612	38	1.9854	1.0102	277
0.4485	6.771	−38	1.3867	1.2478	716	0.9139	1.633	20	2.0904	1.0034	171
T = 313.15 K											
0.1032	10.440	23	1.0413	2.9410	384	0.5540	7.455	−39	1.5061	1.1328	655
0.1962	10.057	79	1.1127	1.9982	577	0.6409	6.502	−7	1.6240	1.0765	576
0.2656	9.659	21	1.1763	1.6580	660	0.7355	5.209	3	1.7622	1.0372	460
0.3512	9.119	−30	1.2640	1.4092	709	0.8550	3.212	41	1.9521	1.0099	275
0.4488	8.413	−41	1.3746	1.2413	709	0.9140	2.028	41	2.0524	1.0033	169
T = 318.15 K											
0.1033	12.955	23	1.0388	2.8348	375	0.5544	9.159	−38	1.4861	1.1284	644
0.1965	12.424	72	1.1071	1.9570	565	0.6413	7.965	−6	1.5990	1.0739	566
0.2658	11.946	35	1.1683	1.6339	647	0.7358	6.357	−3	1.7310	1.0359	452
0.3516	11.259	−24	1.2530	1.3952	697	0.8552	3.914	50	1.9113	1.0096	270
0.4492	10.348	−53	1.3596	1.2333	697	0.9141	2.466	44	2.0060	1.0032	166
T = 323.15 K											
0.1034	15.932	26	1.0369	2.7506	368	0.5550	11.159	−45	1.4702	1.1247	636
0.1967	15.249	90	1.1028	1.9231	557	0.6418	9.687	−4	1.5793	1.0717	559
0.2661	14.637	41	1.1621	1.6140	638	0.7362	7.697	−23	1.7062	1.0348	446
0.3520	13.779	−23	1.2443	1.3835	688	0.8555	4.753	69	1.8789	1.0093	266
0.4497	12.631	−67	1.3478	1.2266	688	0.9143	3.006	67	1.9693	1.0031	164
1-Bromobutane (1) + 1-Decanol (2)											
T = 283.15 K											
0.0997	2.389	26	1.0585	3.1684	391	0.6516	1.469	37	1.6585	1.0593	503
0.1937	2.301	13	1.1444	1.9782	567	0.7095	1.256	10	1.7314	1.0381	438
0.3007	2.172	−1	1.2532	1.4913	654	0.7113	1.228	−12	1.7337	1.0375	436
0.4342	1.913	−50	1.3996	1.2283	658	0.7801	0.977	−16	1.8222	1.0200	347
0.4912	1.833	−15	1.4652	1.1645	634	0.7906	0.940	−13	1.8359	1.0179	333
0.5656	1.697	25	1.5534	1.1051	583	0.9006	0.508	20	1.9824	1.0036	168

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) + 1-Decanol (2) (Continued)											
T = 288.15 K											
0.0998	3.133	23	1.0582	3.0621	389	0.6517	1.859	6	1.6299	1.0549	491
0.1937	3.025	17	1.1426	1.9259	562	0.7096	1.601	−6	1.6967	1.0351	426
0.3007	2.840	−10	1.2482	1.4626	645	0.7114	1.595	−5	1.6988	1.0346	424
0.4343	2.546	−17	1.3882	1.2136	646	0.7802	1.277	2	1.7792	1.0184	337
0.4913	2.393	−15	1.4501	1.1535	621	0.7907	1.237	14	1.7915	1.0164	323
0.5657	2.173	1	1.5326	1.0977	571	0.9007	0.644	21	1.9226	1.0033	163
T = 293.15 K											
0.0998	4.068	34	1.0518	2.9967	378	0.6518	2.405	8	1.6171	1.0564	495
0.1938	3.917	29	1.1321	1.9241	553	0.7097	2.088	6	1.6849	1.0362	431
0.3008	3.677	−2	1.2351	1.4677	641	0.7116	2.077	6	1.6871	1.0356	428
0.4344	3.272	−38	1.3739	1.2177	646	0.7803	1.665	11	1.7692	1.0190	341
0.4914	3.085	−25	1.4358	1.1568	623	0.7908	1.593	7	1.7818	1.0170	327
0.5658	2.802	−5	1.5187	1.1001	574	0.9007	0.821	12	1.9165	1.0034	165
T = 298.15 K											
0.0998	5.232	36	1.0483	2.9052	369	0.6519	3.057	3	1.5955	1.0551	490
0.1938	5.021	27	1.1254	1.8959	543	0.7098	2.660	10	1.6610	1.0353	426
0.3009	4.713	−2	1.2252	1.4561	632	0.7117	2.646	10	1.6632	1.0348	424
0.4345	4.210	−21	1.3600	1.2126	639	0.7805	2.124	21	1.7422	1.0185	338
0.4916	3.945	−28	1.4200	1.1532	616	0.7909	2.023	6	1.7543	1.0166	324
0.5660	3.558	−24	1.5003	1.0978	567	0.9008	1.035	8	1.8838	1.0033	163
T = 303.15 K											
0.0998	6.689	75	1.0440	2.8194	359	0.6521	3.858	2	1.5774	1.0550	488
0.1939	6.331	−6	1.1173	1.8767	533	0.7100	3.342	−4	1.6421	1.0353	425
0.3010	5.986	16	1.2139	1.4511	624	0.7120	3.346	18	1.6443	1.0348	422
0.4347	5.337	−13	1.3456	1.2115	633	0.7806	2.668	14	1.7225	1.0185	337
0.4918	4.978	−42	1.4045	1.1527	611	0.7910	2.564	18	1.7344	1.0166	323
0.5661	4.500	−26	1.4835	1.0977	564	0.9008	1.316	19	1.8626	1.0033	163
T = 308.15 K											
0.0999	8.423	67	1.04337	2.73896	356	0.6524	4.796	−7	1.5552	1.0517	478
0.1940	8.041	45	1.11526	1.83672	527	0.7102	4.148	−10	1.6154	1.0331	415
0.3011	7.522	6	1.20920	1.42924	616	0.7122	4.158	25	1.6175	1.0326	413
0.4350	6.666	−45	1.33603	1.20028	623	0.7809	3.312	24	1.6899	1.0173	329
0.4920	6.241	−45	1.39220	1.14426	600	0.7912	3.176	23	1.7008	1.0155	315
0.5664	5.626	−26	1.46694	1.09204	553	0.9009	1.644	45	1.8183	1.0031	159
T = 313.15 K											
0.1000	10.518	69	1.0416	2.6644	351	0.6527	5.920	−17	1.5365	1.0498	471
0.1942	10.079	100	1.1113	1.8072	521	0.7104	5.116	−18	1.5940	1.0319	410
0.3014	9.339	−22	1.2026	1.4151	608	0.7126	5.136	33	1.5961	1.0313	407
0.4354	8.287	−48	1.3256	1.1935	615	0.7812	4.077	25	1.6650	1.0166	324
0.4924	7.738	−61	1.3799	1.1393	593	0.7914	3.930	44	1.6753	1.0149	311
0.5667	6.970	−32	1.4518	1.0888	546	0.9010	2.034	68	1.7866	1.0029	156
T = 318.15 K											
0.1000	13.048	95	1.0379	2.5777	339	0.6531	7.266	−20	1.5179	1.0495	466
0.1944	12.412	83	1.1038	1.7843	508	0.7116	6.290	7	1.5752	1.0315	405
0.3016	11.532	−3	1.1917	1.4080	597	0.7130	6.286	27	1.5766	1.0312	404
0.4358	10.198	−52	1.3114	1.1914	606	0.7816	4.978	12	1.6445	1.0165	321
0.4928	9.514	−69	1.3644	1.1381	585	0.7916	4.800	32	1.6544	1.0149	308
0.5670	8.566	−34	1.4347	1.0882	540	0.9012	2.501	89	1.7641	1.0029	155
T = 323.15 K											
0.1002	16.044	122	1.0356	2.4949	331	0.6536	8.809	−32	1.4977	1.0479	458
0.1946	15.207	92	1.0988	1.7532	497	0.7112	7.623	−11	1.5518	1.0307	399
0.3020	14.104	0	1.1835	1.3941	586	0.7135	7.606	23	1.5540	1.0301	396
0.4364	12.440	−53	1.2992	1.1852	595	0.7820	6.030	20	1.6188	1.0160	315
0.4934	11.586	−81	1.3502	1.1336	575	0.7919	5.818	50	1.6283	1.0144	303
0.5675	10.419	−35	1.4179	1.0854	531	0.9013	3.037	124	1.7328	1.0028	153

Table 3. Wilson Parameters and Standard Deviations $\sigma(P)$ of Eq 2

	1-bromobutane (1) + 1-octanol (2)			1-bromobutane (1) + 1-decanol (2)		
T/K	Λ_{12}	Λ_{21}	σ/Pa	Λ_{12}	Λ_{21}	σ/Pa
278.15	0.9827	0.0778	9			
283.15	1.0266	0.0720	10	1.2029	0.0644	25
288.15	1.0292	0.0838	12	1.2482	0.0638	14
293.15	1.0465	0.0919	13	1.2281	0.0810	20
298.15	1.0466	0.1081	18	1.2388	0.0912	20
303.15	1.0579	0.1144	25	1.2340	0.1061	30
308.15	1.0650	0.1252	34	1.2684	0.1070	37
313.15	1.0777	0.1338	41	1.2860	0.1131	53
318.15	1.0931	0.1450	42	1.2817	0.1291	56
323.15	1.1056	0.1542	55	1.2940	0.1393	70

Table 4. Experimental Molar Excess Enthalpies and Excess Volumes at T = 298.15 K for 1-Bromobutane (1) + 1-Octanol (2)

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}
0.0250	364	0.3205	1057	0.0702	0.104	0.6922	0.142
0.0571	602	0.3670	1056	0.1016	0.127	0.7908	0.111
0.1224	840	0.4661	1005	0.2062	0.167	0.8530	0.081
0.1949	976	0.5784	889	0.2980	0.183	0.8904	0.057
0.2361	1021	0.7064	692	0.3954	0.187		
0.2760	1048	0.8484	400	0.4953	0.182		
		0.9311	204	0.5976	0.168		

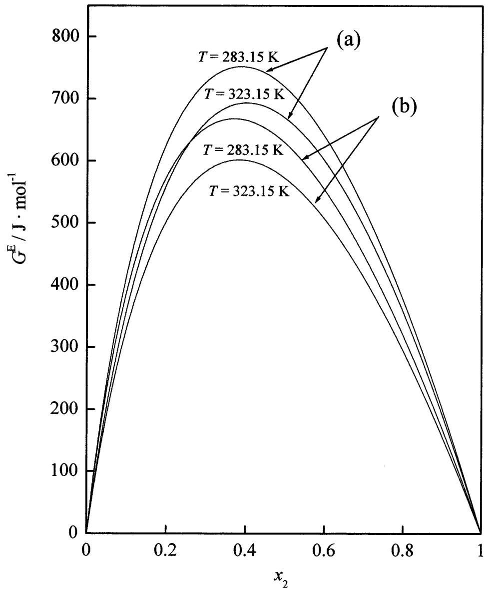

Figure 2. Excess molar Gibbs energies G^E at 283.15 K and 323.15 K plotted as a function of mole fraction of alcohol: (a) {(x_1)1-bromobutane + (x_2)1-octanol}; (b) {(x_1)1-bromobutane + (x_2)1-decanol}..

Table 5. Coefficients C_j and Standard Deviations $\sigma(Q^E)$ for Least-Squares Representation by Eq 10 of H^E and V^E for 1-Bromobutane (1) + 1-Octanol (2), at T = 298.15 K

Q^E	C_0	C_1	C_2	C_3	$\sigma(Q^E)$
H^E/J·mol^{-1}	21881	−60622	70042	−28646	16
V^E/cm^3·mol^{-1}	3.247	−8.593	9.972	−4.040	0.002

Experimental excess molar enthalpies and volumes, at 298.15 K, for mixtures (1-bromobutane + 1-octanol) are given in Table 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 are the mole fractions of 1-bromobutane and alcohol, respectively. For alcohol mixtures, this polynomial[21,22] represents the experimental behavior better than the classical Redlich−Kister equation. Table 5 gives the C_j coefficients along with the standard deviations.

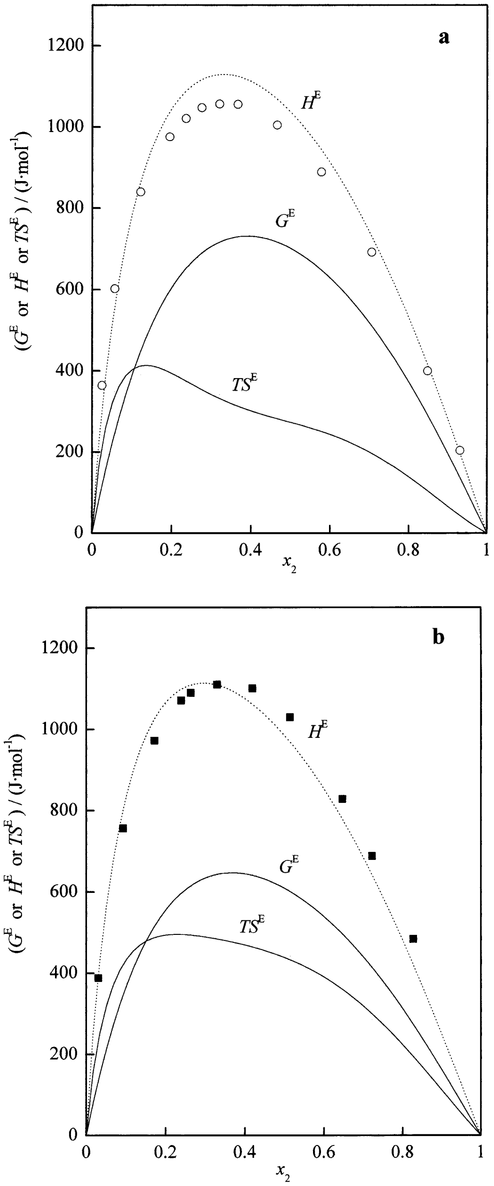

Figure 3. Thermal excess molar functions at T = 298.15 K: (a) {(x_1)1-bromobutane + (x_2)1-octanol}; ○, experimental H^E; (b) {(x_1)1-bromobutane + (x_2)1-decanol}; ■, experimental H^E (Pérez et al.[23]). ···, Gibbs−Helmholtz H^E; —, G^E and TS^E.

Table 6. Thermodynamic Excess Functions for (0.5)Alkanol + (0.5)1-Bromobutane or (0.5)1-Chlorobutane or (0.5)*n*-Hexane at 298.15 K

	1-bromobutane			1-chlorobutane			*n*-hexane[e]		
alcohol	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})
ethanol	772[a]	−419[b]	0.184[a]	706[c]	−437[d]	0.136[c]	555	−850	0.41
1-butanol	956[f]	−3[f]	0.141[f]	873[c]	−65[g]	0.061[c]	510	−630	0.08
1-hexanol	958[a]	147[b]	0.157[a]	905[c]	121[d]	0.030[c]	465	−515	−0.16
1-octanol	977[h]	274[h]	0.182[h]	927[c]	241[i]	0.021[c]	415	−430	−0.35
1-decanol	1031[a]	420[h]	0.200[a]	1002[c]	405[i]	0.041[c]	386[j]	−330[k]	−0.574[c]

[a] Pérez et al.[23] [b] Garriga et al.[8] [c] Pérez et al.[25] [d] Garriga et al.[4] [e] Brown et al.[26] [f] Garriga et al.[6] [g] Garriga et al.[2] [h] This work. [i] Garriga et al.[5] [j] Kumaran et al.[27] [k] Wieczorek.[28]

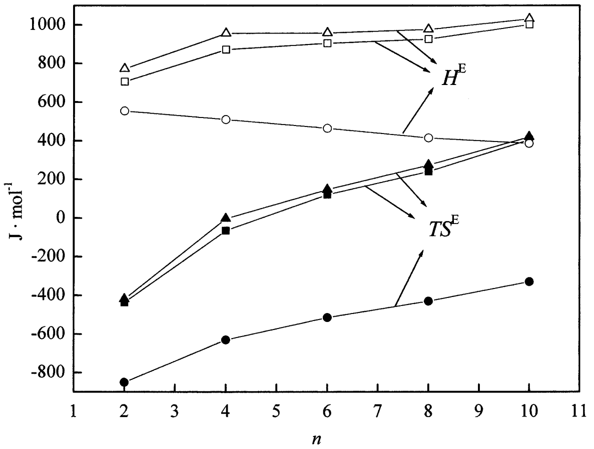

Figure 4. Excess molar enthalpies and entropies, at $T = 298.15$ K and $x = 0.5$, for mixtures of a straight-chain alcohol of *n* carbon atoms with solvent: △, 1-bromobutane; □, 1-chlorobutane; O, *n*-hexane (empty symbols, enthalpies;full symbols, entropies). See Table 6 for source of data.

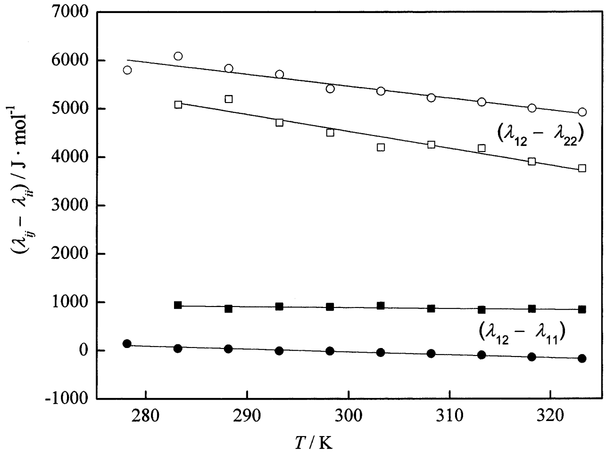

Figure 5. Wilson coefficients as a function of temperature for binary mixtures of {(x_1)1-bromobutane + (x_2)1-octanol} [●, ($\lambda_{12} - \lambda_{11}$); ○, ($\lambda_{12} - \lambda_{22}$)] and of {($x_1$)1-bromobutane + ($x_2$)1-decanol} [■, ($\lambda_{12} - \lambda_{11}$); □, ($\lambda_{12} - \lambda_{22}$)].

We tested 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 calculated H^E values at $T = 298.15$ K are shown as curves in Figure 3. A good agreement is obtained considering that the quantitative evaluation of H^E from vapor pressures involves considerable uncertainty.[24] In the same figure and at the same temperature, TS^E curves (obtained from $TS^E = H^E - G^E$) are also plotted.

H^E, TS^E, and V^E at $T = 298.15$ K and $x = 0.5$ are collected in Table 6. For mixtures of a straight-chain alkanol + 1-bromobutane or + 1-chlorobutane as a polar solvent, H^E and TS^E are plotted in Figure 4 and are compared with those for mixtures containing *n*-hexane as an inert solvent. Excess molar enthalpies and entropies are much more positive than those for inert solvent solutions due to the interaction between the OH group and the polar group. On the other hand, in mixtures of an alkanol with 1-bromobutane or 1-chlorobutane, a similar behavior is observed for both thermodynamic excess functions. The effect of the chain length of the alcohol will be due to formation of contacts between the halogen atom and the chain of the alcohol, and at a given composition, it will be larger in solutions of longer chain alcohols. The volumetric behavior is a more complicated question as is the result of both structural and interaction effects.

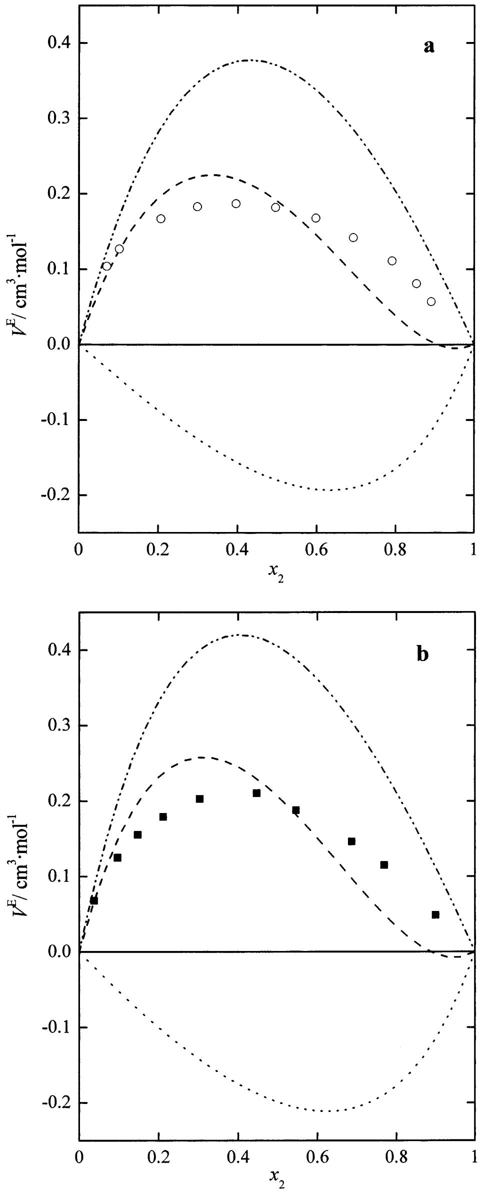

Figure 6. Excess molar volumes V^E of (a) {(x_1)1-bromobutane + (x_2)1-octanol} and (b) {(x_1)1-bromobutane + (x_2)1-decanol}, at $T = 298.15$ K: ○, this work; ■, Pérez et al.;[23] ···, chemical contribution; -···-, physical contribution; —, ERAS model.

The constants λ_{ij}, defined as negative values, stand for the energies of interaction between the molecules designated in the subscripts. The Wilson coefficients ($\lambda_{ij} - \lambda_{jj}$) are plotted in Figure 5 as a function of temperature. According to Wilson's equation, to a fair approximation, the differences in the characteristic energies are independent of the temperature, at least over modest temperature intervals. For accurate work, these differences may depend on the temperature, as shown in Figure 5 for ($\lambda_{12} - \lambda_{22}$).

A theoretical approach developed by Heintz[29]—the so-called extended real associated solution (ERAS) model—combines Flory's theory[30] for chainlike molecules with the Kretschmer and Wiebe linear association model[31] and makes it possible to calculate G^E, H^E, and V^E. We have tested the ERAS model of Heintz (original version) for a set of mixtures of 1-bromobutane + an alcohol[32] ranging from 2 to 10 carbon atoms. For alcohols, the self-association parameters used for enthalpy and volume were $\Delta h_2^* =$

-25.1 kJ·mol^{-1}, $\Delta v_2^* = -5.6$ cm^3·mol^{-1}, and the equilibrium constants $K_2 = 98$ for 1-octanol and $K_2 = 88$ for 1-decanol. We have calculated the enthalpy and volume cross-association parameters by fitting, simultaneously, our experimental results of G^E, H^E, and V^E, for eight mixtures including branched alkanols of 1-bromobutane + alcohol, obtaining $\Delta h_{12}^* = -13.0$ kJ·mol^{-1} and $\Delta v_{12}^* = -5.8$ cm^3·mol^{-1}, which characterize the (OH) ↔ Br interaction.[8] These values are similar to those obtained for the (OH) ↔ Cl interaction ($\Delta h_{12}^* = -14.5$ kJ·mol^{-1} and $\Delta v_{12}^* = -6.5$ cm^3·mol^{-1}).[5] While holding these values constant, we adjusted the other cross parameters K_{12}, X_{12}, and Q_{12} to fit the experimental data for each mixture. For mixtures of alcohol and a polar solvent, the ERAS model satisfactorily reproduces the experimental curves of H^E and G^E. However, for V^E, the agreement is poor, as shown in Figure 6. The failure to reproduce the V^E curves has been observed with other polar solvents[33] (except ether),[34,35] and the disagreement is more noticeable with short chain alcohols.

Literature Cited

(1) Scheiner, S. *Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997; p 11.

(2) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Isothermal (vapour + liquid) equilibrium at several temperatures of (1-chlorobutane + 1-butanol, or 2-methyl-2-propanol). *J. Chem. Thermodyn.* **2001**, *33*, 523−534.

(3) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Thermodynamic excess properties for binary mixtures of 1-chlorobutane with 2-butanol or 2-methyl-1-propanol. *Fluid Phase Equilib.* **2001**, *181*, 203-214.

(4) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. Isothermal Vapor-Liquid Equilibrium of 1-Chlorobutane with Ethanol or 1-Hexanol at Ten Temperatures between 278.15 K and 323.15 K. *J. Chem. Eng. Data* **2001**, *46*, 535−540.

(5) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Isothermal (vapour + liquid) equilibrium at several temperatures of (1-chlorobutane + 1-octanol, or 1-decanol). *J. Chem. Thermodyn.*, in press, JCT03/027.

(6) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. 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. *J. Chem. Eng. Data* **2002**, *47*, 322−328.

(7) Martínez, S.; Garriga, R.; Pérez, P.; Gracia, M. 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. *J. Chem. Eng. Data* **2003**, *48*, 294−301.

(8) Garriga, R.; Martínez, S.; Pérez, P.; Gracia, M. Vapour pressures at 10 different temperatures between 278.15 K and 323.15 K for binary mixtures of 1-bromobutane with ethanol or 1-hexanol. *Fluid Phase Equilib.* **2003**, *207*, 97−109.

(9) Marsh, K. N. Thermodynamics of octamethylcyclotetrasiloxane mixtures. *Trans. Faraday Soc.* **1968**, *64*, 883−893.

(10) Pardo, J.; Pérez, P.; Royo, F.; Gracia, M.; Gutiérrez Losa, C. $H_m{}^E$, $V_m{}^E$ and $G_m{}^E$ of {x$Cl_2HCCHCl_2$ + (1-x)C_6H_{14}} at Several Temperatures. *J. Chem. Thermodyn.* **1987**, *19*, 521−526.

(11) Gracia, M.; Sánchez, F.; Pérez, P.; Valero, J.; Gutiérrez Losa, C. Vapour Pressures of (Butan-1-ol + Hexane) at Temperatures Between 283.10 and 323.12 K. *J. Chem. Thermodyn.* **1992**, *24*, 463−471.

(12) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1973**, *1*, 23.

(13) Timmermans, J. *Physico−Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950; Vol. 1, p 265; 1965; Vol. 2, p 208.

(14) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*; Wiley: New York, 1986; p 529.

(15) *TRC Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1966; d-5000.

(16) *TRC Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1976; k-5001.

(17) Velasco, I. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1987**, *4*, 255.

(18) Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, *20*, 263−272.

(19) Barker, J. A. Determination of Activity Coefficients from Total Pressure Measurements. *Aust. J. Chem.* **1953**, *6*, 207−210.

(20) Wilson, G. M. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(21) Ottesstedt, E. A.; Missen, R. W. Thermodynamic Properties of Solutions of Alcohols and Carbon Tetrachloride. *Trans. Faraday Soc.* **1962**, *58*, 879−889.

(22) Treszczanowicz, A. J.; Benson, G. C. Excess volumes for *n*-alkanols + *n*-alkanes. I. Binary mixtures of methanol, ethanol, *n*-propanol, and *n*-butanol + *n*-heptane. *J. Chem. Thermodyn.* **1977**, *9*, 1189−1197.

(23) Pérez, P.; Gracia, M.; Gutiérrez Losa, C. $H_m{}^E$ y $V_m{}^E$ de mezclas binarias 1−bromobutano + n−alcohol. *Rev. Acad. Cienc. Zaragoza* **1988**, *43*, 201−206.

(24) Rowlinson, J. S.; Swinton, F. L. *Liquids and Liquids Mixtures*, 3rd ed.; Butterworth: London, 1982; p 138.

(25) Pérez, P.; Royo, F.; Gracia, M.; Gutiérrez Losa, C. $H_m{}^E$ and $V_m{}^E$ of some (1-chlorobutane + alkanol or cyclohexanol) mixtures. *J. Chem. Thermodyn.* **1985**, *17*, 711−718.

(26) Brown, I.; Fock, W.; Smith, F. *J.* The thermodynamic properties of solutions of normal and branched alcohols in benzene and *n*-hexane. *J. Chem. Thermodyn.* **1969**, *1*, 273−291.

(27) Kumaran, M. K.; Benson, G. C. Excess enthalpies of decan-1-ol + *n*-pentane, + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-nonane, + *n*-decane, and + *n*-undecane at 298.15 K. *J. Chem. Thermodyn.* **1984**, *16*, 175−182.

(28) Wieczorek, S. A. Vapour pressures and thermodynamic properties of decan-1-ol + *n*-hexane between 283.160 and 333.151 K. *J. Chem. Thermodyn.* **1979**, *11*, 239−245.

(29) Heintz, A. A New Theoretical Approach for Predicting Excess Properties of Alkanol/Alkane Mixtures. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 172−181.

(30) Flory, P. J.; Orwoll, R. A.; Vrij, A. Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3507−3514.

(31) Kretschmer, C. B.; Wiebe, R. Thermodynamics of Alcohol-Hydrocarbon Mixtures. *J. Chem. Phys.* **1954**, *22*, 1697−1701.

(32) Martínez, S. Thesis, University of Zaragoza, Spain, 2002.

(33) Garriga, R. Thesis, University of Zaragoza, Spain, 1998.

(34) Garriga, R.; Pérez, P.; Gracia, M. Vapour Pressures at Eight Temperatures of Mixtures of Di-*n*-propyl Ether + Ethanol or 1-Butanol − Thermodynamic Description of Mixtures of Di-*n*-propyl Ether + Alkanol According to the ERAS−Model. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 1466−1473.

(35) Garriga, R.; Sánchez, F.; Pérez, P.; Gracia, M. Vapour Pressures at Several Temperatures of Binary Mixtures of Di-*n*-propyl Ether + 2-Methyl-1-propanol or 2-Methyl-2-propanol, and Excess Functions, at $T = 298.15$ K. Thermodynamic Description According to the ERAS−Model. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 14−24.

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