J. Chem. Eng. Data **2009,** *54,* 2045–2048

Isothermal Vapor−Liquid Equilibria and Excess Enthalpy Data for the Binary System (Butyric Acid + Toluene)

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The vapor pressures of (butyric acid + toluene) and of the pure components were measured by means of a static device at temperatures between (273 and 363) K. The data were correlated with the Antoine equation. From these data, excess Gibbs functions were calculated for several constant temperatures and fitted to a fourth-order Redlich−Kister equation. The system shows positive deviation from ideality. Additionally, molar excess enthalpies, H^E, for the binary (butyric acid + toluene) system have been measured at 323.15 K using an isothermal flow calorimeter.

Introduction

Vapor−liquid equilibrium (VLE) data are essential for the design of separation processes and equipment as well as for the extension of thermodynamic models. The present paper is part of a research program on (vapor−liquid) equilibria (VLE) and excess enthalpies (H^E) in mixtures containing carboxylic acids. The purpose of the present work is to investigate VLE and H^E of (butyric acid + toluene) with a view to use the results to determine interaction parameters for predictive group contribution methods. A survey of the literature[1−6] shows that VLE or H^E data available for the butyric acid + toluene binary system are scarce. According to the Dortmund Data Bank (DDB),[6] there is only one data set available for this system (at atmospheric pressure).[7]

Experimental Section

The substances were supplied by Aldrich Chem. (Milwaukee, WI, USA). They were used without further purification. The purities, tested by GLC, were: butyric acid (Aldrich, > 99 %), toluene (Aldrich, > 99.5 %). The experimental vapor pressure (p) data were obtained with an apparatus described in detail by Blondel-Telouk and co-workers[8,9] as a function of the temperature (T) for constant mole fraction composition (x_i). The apparatus allows measurements at pressures from (27 to $200 \cdot 10^3$) Pa and at temperatures from (258.15 to 468.15) K. The pressure was measured with a pressure gauge (Rosemount, model 1151 DPE 22S2, Minneapolis, MN), separated from the working fluid by a differential pressure indicator (MKS, model 615D, MKS Instruments, USA). The pressure gauges were periodically checked against a Hg or oil manometer and a Bouty (Paris, France) type 70298 cathetometer, which when combined provide pressures with an uncertainty of 1 Pa. The temperature of the oil-filled thermostat was maintained constant to ± 0.01 K. The temperature was measured by means of a copper−constantan thermocouple calibrated against a Leeds and Northrup standard platinum resistance thermometer 8163-B, calibrated by the National Bureau of Standards (Washington, DC) and connected to a Mueller type G2 bridge (with a precision 10^{-4} Ω). All temperatures are reported on ITS-90. The estimated uncertainties in pressure, temperature, and mole fraction are as follows: $\sigma(p) = 0.15(p/\mathrm{Pa})$ for $p < 13.3$ Pa, $\sigma(p) = 0.05(p/\mathrm{Pa})$ at pressure between (13.3 and 200) Pa, $\sigma(p) = 0.005(p/\mathrm{Pa})$ in the range (200 to 1000) Pa, $\sigma(p) = 0.002(p/\mathrm{Pa})$ for the range (1000 to $200 \cdot 10^3$) Pa, $\sigma(T) = 0.01$ K, and $\sigma(x_i) = 0.0002$. Mixtures were prepared by mass and thoroughly degassed by distillation as described by Blondel-Tellouk and co-workers.[8,9] The final composition of the liquid was determined after each pressure measurement by gas−liquid chromatography with a column filled with a stationary phase of Carbowax and a thermal conductivity detector.

A commercially available isothermal flow calorimeter from Hart Scientific (model 7501) was used for the excess enthalpy measurements.[10] The calorimeter consists of two solvent pumps (ISCO, LC 2600, 260 cm^3); a thermostatted flow cell; and a back pressure regulator, which prevents evaporation (it is known[11] that vaporization effects may cause considerable errors at higher temperatures) and provides the opportunity to measure H^E data also at higher pressures (up to 15 MPa). The flow cell (containing a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder[12]) is located in a stainless steel cylinder that is immersed in a thermostat. The power per pulse can be varied between (0.05 and 20) μJ. The exact energy per pulse is obtained by calibration using the energy dissipated from a precise resistor fixed at the cylinder of the flow cell. The temperature of the flow cell, T, is maintained constant by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler and the heat effect. The temperature of the liquid pumps and the thermostat is monitored with Hart Scientific platinum resistance thermometers (model 1006 Micro-Therm) with an uncertainty

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10.1021/je800888n CCC: $40.75

Table 1. Coefficients A, B, and C and Overall Mean Relative Deviation in Pressure of the Antoine Equation (Equation 1)[a]

compound	temperature/K	A	B	C	$100(\delta P/P)$
butyric acid	293.29 to 363.08	8.94748	2440.79	244.6572	0.28
toluene	253.83 to 363.08	7.14586	1448.97	229.5312	0.14

[a] $100\delta P/P = (1/N)\sum_{i=1}^{N} 100((P_{\text{calcd}} - P_{\text{exptl}})/P_{\text{exptl}})$, where N is the total number of experimental values.

of ± 0.005 K. From the recorded frequency change of the pulsed heater, the flow rate, the pure component densities, and the molar mass of the components, x_i, the molar excess enthalpies can be calculated using the energy evolved per pulse. The experimental uncertainties associated to the experiments performed with this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(H^{\text{E}}) = 2\ \text{J}\cdot\text{mol}^{-1} + 0.01\ (H^{\text{E}}/\text{J}\cdot\text{mol}^{-1})$, $\sigma(x_i) = 0.0001$.

Results and Discussion

The experimental vapor pressure data were fitted to the Antoine equation, where $P° = 1$ mmHg

$$\log_{10} P/P° = A - \frac{B}{C + t(°C)} \tag{1}$$

The objective function Q was the sum of the squared relative deviations in pressure

$$Q = \sum \left(\frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}}\right)^2 \tag{2}$$

The overall mean relative deviation in pressure is

$$100\frac{\delta P}{P} = \frac{100}{N}\sum_{i=1}^{N}\left(\frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}}\right) \tag{3}$$

where N is the total number of experimental values, and is less than 0.1 %.

Table 1 lists for the pure components butyric acid and toluene the temperature range; the coefficients A, B, and C of the Antoine equation; and the overall mean relative deviation in pressure.

The experimental and calculated vapor pressures of pure butyric acid and toluene are listed in Table 2.

For pure butyric acid, our vapor pressure data agree to within 1 % with those reported in the literature by Jasper et al.[13] in the temperature range (293 to 363) K and 0.4 % with Dreisbach et al.[14] at 363 K. For toluene, our vapor pressure data agree with those reported in the literature[15] within 0.05 %.

The vapor pressure at several different temperatures as a function of the mole fraction for the binary mixture, shown in Figure 1, is also listed in Table 3.

For the binary mixture, the vapor pressures were measured at temperatures between (273.15 and 363.15) K, and the results were fitted to the Antoine equation. The molar excess Gibbs functions G^{E} were estimated from the Redlich−Kister[16] equation using the method of Barker[17]

$$G^{\text{E}} = x_1(1 - x_1)\sum_{j=1}^{m} RTG_j(2x_1 - 1)^{j-1} \tag{4}$$

where x_1 is the molar fraction for butyric acid. The coefficients G_j were determined by regression through minimization of the sum of deviations in pressure. Vapor-phase imperfection and the variation of Gibbs function of the pure liquid components with pressure were accounted for in terms of the second molar virial coefficients, estimated by the method of Tsonopoulos,[18,19] and the molar volumes under saturation pressure.

Table 2. Experimental and Calculated with the Antoine Equation (Equation 1) Vapor Pressures of Pure Butyric Acid and Toluene[a]

T/K	P(exptl)/Pa	P(from eq 1)/Pa	$100\delta P/P$
	Butyric Acid		
293.29	72.0	71.6	0.61
298.25	105.2	105.7	−0.51
303.28	154.5	154.9	−0.25
313.22	315.5	316.2	−0.22
323.20	618.3	616.9	0.23
333.18	1153.4	1152.1	0.11
343.18	2073.4	2070.9	0.12
353.10	3581.8	3574.7	0.20
363.08	5973.2	5990.3	−0.29
$100\delta P/P$			0.28
	Toluene		
253.83	239.2	238.7	0.20
263.64	483.7	484.3	−0.12
273.47	925.4	926.3	−0.10
283.32	1680.0	1682.5	−0.15
293.24	2925.5	2924.3	0.04
293.26	2925.5	2928.2	−0.09
298.25	3802.9	3804.4	−0.04
303.23	4894.3	4892.5	0.04
313.19	7871.5	7866.3	0.07
313.22	7874.1	7874.9	−0.01
323.22	12244.0	12261.0	−0.14
333.20	18574.0	18497.0	0.42
343.16	27202.0	27131.0	0.26
353.13	38837.0	38835.0	0.00
363.08	54133.0	54339.0	−0.38
$100\delta P/P$			0.14

[a] $100\delta P/P = (1/N)\sum_{i=1}^{n} 100((P_{\text{calcd}} - P_{\text{exptl}})/P_{\text{exptl}})$.

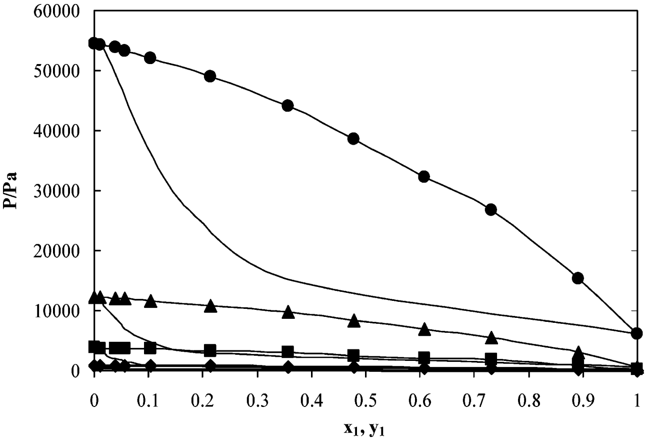

Figure 1. Experimental and calculated $P-x(y)$ behavior of the system butyric acid (1) + toluene (2) at different temperatures: ◆, 273.15 K; ■, 298.15 K; ▲, 323.15; ●, 363.15 K; −, calculated values using Barker's method.

Table 3 also lists for (butyric acid + toluene) the corresponding compositions of the liquid and vapor phases, the activity coefficients γ_1 and γ_2, and the values of the excess molar Gibbs functions G^{E} calculated by Barker's method, using the Redlich−Kister equation.

For the investigated binary mixture, the molar excess Gibbs functions G^{E} at different temperatures, calculated from our vapor pressure data, are plotted in Figure 2 against the mole fraction x_1 of butyric acid.

The binary mixture (butyric acid + toluene) does not show azeotropic behavior. It exhibits positive deviations in G^{E} values calculated from the vapor pressure data. The equimolar G^{E} of (butyric acid + toluene) decreases with increasing temperature from 546 J·mol^{-1} at $T = 273.15$ K to 531 J·mol^{-1} at $T =$

Table 3. Values of the Vapor Pressure P, Standard Deviations $100\delta P/P$, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Functions G^E for the Binary System Butyric Acid (1) + Toluene (2)

x_1	y_1	P/Pa	$100\delta P/P$	γ_1	γ_2	G^E/J·mol^{-1}	x_1	y_1	P/Pa	$100\delta P/P$	γ_1	γ_2	G^E/J·mol^{-1}
$T = 273.15$ K													
0.0000	0.0000	908.2	0.00	7.2880	1.0000	0.0	0.3565	0.0095	706.9	0.07	1.3723	1.1976	519.8
0.0115	0.0011	901.1	0.18	6.1543	1.0010	49.6	0.4791	0.0142	607.7	1.33	1.2949	1.2502	545.3
0.0386	0.0026	895.8	1.32	4.3584	1.0097	150.2	0.6072	0.0188	507.6	−1.68	1.1663	1.4208	525.5
0.0572	0.0032	874.7	−0.14	3.5762	1.0198	207.5	0.7324	0.0236	447.1	0.83	1.0436	1.7829	422.4
0.1041	0.0041	855.2	−0.65	2.4428	1.0538	317.8	0.8926	0.0537	224.1	−0.12	0.9882	2.1794	165.9
0.2134	0.0056	813.3	−0.52	1.5780	1.1381	452.1	1.0000	1.0000	13.7	0.00	1.0000	1.5948	0.0
$T = 283.15$ K													
0.0000	0.0000	1665.8	0.00	6.6778	1.0000	0.0	0.3565	0.0119	1300.3	0.07	1.3363	1.1984	517.5
0.0115	0.0013	1655.2	0.30	5.7045	1.0009	49.2	0.4791	0.0178	1115.4	1.05	1.2609	1.2504	535.5
0.0386	0.0032	1646.9	1.55	4.1303	1.0091	149.4	0.6072	0.0242	925.4	−1.27	1.1501	1.3992	510.5
0.0572	0.0040	1612.9	0.43	3.4286	1.0186	206.7	0.7324	0.0316	789.5	0.60	1.0434	1.7070	410.2
0.1041	0.0051	1572.0	−0.27	2.3865	1.0509	317.8	0.8926	0.0720	397.8	−0.09	0.9915	2.0692	166.0
0.2134	0.0072	1485.8	−0.68	2.1.554	1.1337	453.8	1.0000	1.0000	32.4	0.00	1.0000	1.6352	0.0
$T = 293.15$ K													
0.0000	0.0000	2910.6	0.00	6.2569	1.0000	0.0	0.3565	0.0149	2280.1	0.06	1.3108	1.1994	520.4
0.0115	0.0016	2895.2	0.39	5.3928	1.0009	49.3	0.4791	0.0222	1954.7	0.83	1.2361	1.2516	532.5
0.0386	0.0040	2882.1	1.69	3.9719	1.0086	149.9	0.6072	0.0308	1615.1	−0.96	1.1380	1.3846	502.8
0.0572	0.0050	2829.0	0.81	3.3266	1.0176	207.7	0.7324	0.0414	1346.9	0.43	1.0432	1.6537	403.7
0.1041	0.0065	2752.0	0.01	2.3492	1.0486	320.4	0.8926	0.0940	684.8	−0.06	0.9941	1.9915	167.4
0.2134	0.0092	2590.4	−0.79	1.5386	1.1304	459.1	1.0000	1.0000	72.5	0.00	1.0000	1.6681	0.0
$T = 298.15$ K													
0.0000	0.0000	3784.6	0.00	6.0953	1.0000	0.0	0.3565	0.0167	2970.6	0.05	1.3011	1.1999	523.3
0.0115	0.0017	3766.2	0.42	5.2727	1.0008	49.4	0.4791	0.0248	2547.1	0.75	1.2265	1.2523	532.9
0.0386	0.0044	3749.7	1.72	3.9107	1.0084	150.5	0.6072	0.0347	2102.2	−0.84	1.1331	1.3792	501.1
0.0572	0.0055	3684.2	0.94	3.2874	1.0172	208.7	0.7324	0.0471	1738.3	0.37	1.0431	1.6335	402.1
0.1041	0.0073	3581.8	0.12	2.3353	1.0477	322.3	0.8926	0.1064	888.7	−0.05	0.9950	1.9615	168.4
0.2134	0.0103	3366.5	−0.83	1.5333	1.1290	462.7	1.0000	1.0000	106.3	0.00	1.0000	1.6809	0.0
$T = 303.15$ K													
0.0000	0.0000	4871.5	0.00	5.9575	1.0000	0.0	0.3565	0.0187	3831.8	0.05	1.2930	1.2003	527.0
0.0115	0.0019	4849.7	0.44	5.1700	1.0008	49.6	0.4791	0.0277	3286.8	0.68	1.2183	1.2530	534.5
0.0386	0.0049	4828.8	1.73	3.8582	1.0083	151.3	0.6072	0.0389	2711.0	−0.73	1.1288	1.3749	500.7
0.0572	0.0062	4748.4	1.04	3.2538	1.0169	209.9	0.7324	0.0532	2226.7	0.31	1.0429	1.6167	401.5
0.1041	0.0082	4614.8	0.21	2.3236	1.0469	324.7	0.8926	0.1198	1145.6	−0.05	0.9959	1.9359	169.5
0.2134	0.0116	4332.5	−0.86	1.5290	1.1278	466.9	1.0000	1.0000	154.1	0.00	1.0000	1.6909	0.0
$T = 313.15$ K													
0.0000	0.0000	7847.8	0.00	5.7327	1.0000	0.0	0.3565	0.0233	6200.4	0.04	1.2809	1.2005	536.0
0.0115	0.0023	7817.4	0.46	5.0014	1.0008	50.2	0.4791	0.0344	5326.6	0.57	1.2055	1.2540	540.1
0.0386	0.0060	7783.5	1.71	3.7709	1.0080	153.2	0.6072	0.0485	4394.1	−0.58	1.1218	1.3686	502.7
0.0572	0.0076	7664.6	1.15	3.1974	1.0163	212.9	0.7324	0.0672	3576.9	0.23	1.0421	1.5913	402.4
0.1041	0.0102	7447.4	0.32	2.3039	1.0455	330.0	0.8926	0.1494	1866.8	−0.03	0.9970	1.8950	171.8
0.2134	0.0146	6982.6	−0.90	1.5227	1.1256	476.0	1.0000	1.0000	312.8	0.00	1.0000	1.5012	0.0
$T = 323.15$ K													
0.0000	0.0000	12218.5	0.00	5.5482	1.0000	0.0	0.3565	0.0288	9699.2	0.05	1.2725	1.1999	545.9
0.0115	0.0029	12176.6	0.45	4.8608	1.0008	50.9	0.4791	0.0424	8351.2	0.50	1.1963	1.2542	547.7
0.0386	0.0074	12121.0	1.62	3.6951	1.0077	155.4	0.6072	0.0560	6900.4	−0.50	1.1163	1.3642	507.3
0.0572	0.0094	11948.6	1.15	3.1471	1.0159	216.1	0.7324	0.0836	5596.4	0.19	1.0409	1.5739	405.0
0.1041	0.0127	11614.8	0.36	2.2849	1.0443	335.6	0.8926	0.1830	2968.8	−0.03	0.9976	1.8628	173.8
0.2134	0.0182	10886.6	−0.92	1.5176	1.1235	485.3	1.0000	1.0000	608.4	0.00	1.0000	1.6968	0.0
$T = 333.15$ K													
0.0000	0.0000	18450.4	0.00	5.3774	1.0000	0.0	0.3565	0.0355	14718.1	0.07	1.2667	1.1980	555.5
0.0115	0.0034	18392.6	0.43	4.7276	1.0007	51.5	0.4791	0.0520	12708.9	0.46	1.1897	1.2530	555.9
0.0386	0.0090	18301.8	1.47	3.6190	1.0075	157.5	0.6072	0.0734	10531.0	−0.49	1.1115	1.3606	512.9
0.0572	0.0115	18055.8	1.06	3.0942	1.0155	219.1	0.7324	0.1024	8546.6	0.19	1.0391	1.5618	408.2
0.1041	0.0156	17567.1	0.34	2.2624	1.0433	340.6	0.8926	0.2204	4616.3	−0.03	0.9977	1.8347	174.7
0.2134	0.0225	16474.3	−0.91	1.5120	1.1212	493.7	1.0000	1.0000	1138.3	0.00	1.0000	1.6756	0.0
$T = 343.15$ K													
0.0000	0.0000	27104.8	0.00	5.1993	1.0000	0.0	0.3565	0.0434	21730.2	0.11	1.2621	1.1945	563.1
0.0115	0.0041	27024.8	0.38	4.5853	1.0007	52.0	0.4791	0.0633	18826.2	0.45	1.1846	1.2500	563.1
0.0386	0.0108	26877.7	1.28	3.5325	1.0074	159.1	0.6072	0.0890	15660.0	−0.52	1.1070	1.3568	518.2
0.0572	0.0139	26531.9	0.89	3.0314	1.0151	221.3	0.7324	0.1238	12764.2	0.22	1.0364	1.5526	410.5
0.1041	0.0190	25846.6	0.26	2.2324	1.0423	344.4	0.8926	0.2614	7029.3	−0.04	0.9972	1.8068	174.0
0.2134	0.0275	24267.8	−0.87	1.5042	1.1185	500.0	1.0000	1.0000	2055.5	0.00	1.0000	1.6359	0.0
$T = 353.15$ K													
0.0000	0.0000	38841.4	0.00	4.9983	1.0000	0.0	0.3565	0.0528	31297.8	0.17	1.2576	1.1892	567.4
0.0115	0.0049	38730.1	0.32	4.4211	1.0007	52.2	0.4791	0.0765	27215.2	0.46	1.1801	1.2446	567.7
0.0386	0.0129	38496.1	1.05	3.4275	1.0072	159.8	0.6072	0.1068	22743.0	−0.61	1.1023	1.3519	521.4
0.0572	0.0165	38015.7	0.66	2.9525	1.0147	222.3	0.7324	0.1478	18674.7	0.28	1.0327	1.5443	410.6
0.1041	0.0228	37092.4	0.15	2.1915	1.0412	346.0	0.8926	0.3060	10496.8	−0.05	0.9961	1.7755	170.9
0.2134	0.0334	34886.9	−0.81	1.4926	1.1152	502.8	1.0000	1.0000	3592.8	0.00	1.0000	1.5759	0.0
$T = 363.15$ K													
0.0000	0.0000	54420.7	0.00	4.7643	1.0000	0.0	0.3565	0.0636	44075.0	0.25	1.2524	1.1817	566.6
0.0115	0.0057	54265.2	0.24	4.2268	1.0007	52.1	0.4791	0.0917	38477.9	0.49	1.1756	1.2366	568.0
0.0386	0.0150	53900.6	0.79	3.2986	1.0070	159.3	0.6072	0.1270	32324.4	−0.75	1.0968	1.3450	520.9
0.0572	0.0194	53240.8	0.37	2.8532	1.0143	221.6	0.7324	0.1744	26806.9	0.38	1.0278	1.5354	407.0
0.1041	0.0269	52042.4	0.00	2.1369	1.0400	344.7	0.8926	0.3537	15392.9	−0.07	0.9945	1.7375	164.4
0.2134	0.0401	49054.0	−0.73	1.4759	1.1111	501.0	1.0000	1.0000	6094.6	0.00	1.0000	1.4943	0.0

Table 4. Experimental Excess Molar Enthalpies of the Binary System Butyric Acid (1) + Toluene (2) at $T = 323.15$ K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0289	27.56	0.3849	−54.1	0.7306	−61.5
0.0576	27.75	0.4366	−62.4	0.7771	−54.2
0.1144	15.39	0.4874	−68.4	0.8230	−44.8
0.1702	−1.51	0.5375	−72.9	0.8682	−33.4
0.2251	−18.11	0.5869	−73.7	0.9127	−22.8
0.2792	−30.59	0.6355	−70.7	0.9567	−10.5
0.3325	−43.64	0.6834	−67.4	0.9784	−4.78

Table 5. Redlich−Kister Parameters (Equation 5)

component 1	component 2	T/K	H_1	H_2	H_3	H_4	$\sigma(H^E)$ (J·mol^{-1})
butyric acid	toluene	323.15	−291.2	−111.8	365.6	−334.4	0.09

298.15 K and increases with increasing temperature from 532 J·mol^{-1} at $T = 303.15$ K to 564 J·mol^{-1} at $T = 363.15$ K.

The experimental molar excess enthalpy H^E of the investigated binary mixture (reported in Table 4) has been fitted to the smoothing equation

$$H^E_{i,\mathrm{exptl}} = x_1(1 - x_1)\sum_{i=0}^{n-1} H_i(2x_1 - 1)^i \qquad (5)$$

The values of the coefficients H_i and the standard deviations $\sigma(H^E)$ (reported in Table 5) are given by

$$\sigma(H^E) = [\sum_{i=1}^{N}(H^E_{i,\mathrm{exptl}} - H^E_{i,\mathrm{calcd}})^2/(N - n)]^{1/2} \qquad (6)$$

where N is the number of experimental points and n is the number of coefficients H_i; they are determined by least-squares analysis.

For (butyric acid + toluene), no comparison was possible for H^E. Figure 3 shows the experimental and calculated excess enthalpy as a function of x_1, the mole fraction of butyric acid for the binary mixture at $T = 323.15$ K.

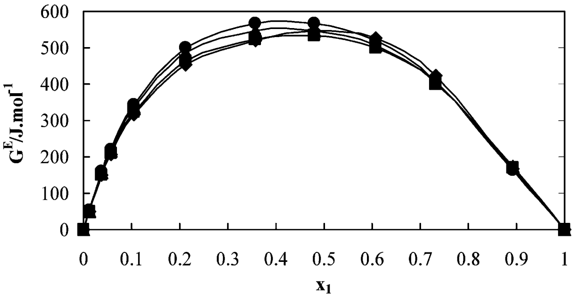

Figure 2. G^E against x_1 for the butyric acid (1) + toluene (2) system: ◆, 273.15 K; ■, 298.15 K; ▲, 323.15 K; ●, 363.15 K; −, calculated values using eq 5.

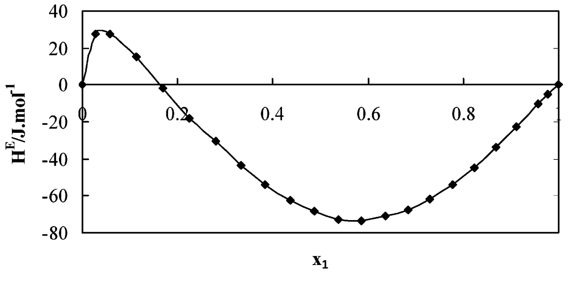

Figure 3. Experimental excess molar enthalpy, H^E, for butyric acid (1) + toluene (2) as a function of the mole fraction, x_1, of butyric acid at 323.15 K.

Summary

Vapor−liquid equilibrium data for the binary mixture of (butyric acid + toluene) were measured at several temperatures using a static device. Deviations from Raoult's law are positive and relatively large. Additionally, excess enthalpy H^E was measured for the same binary mixture at $T = 323.15$ K.

Acknowledgment

The authors thank R. Bölts for technical assistance.

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Received for review November 21, 2008. Accepted April 12, 2009. A part of this work has been done in the framework of an international project (DEF/CNRS n° 15935).

JE800888N