Isobaric Vapor−Liquid Equilibria in the Binary Systems of 1-Bromopropane with Cyclohexane, Heptane, and 1-Butanol

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Vapor−liquid equilibrium at 101.3 kPa has been determined for the binary systems of 1-bromopropane with cyclohexane, heptane, and 1-butanol. The three systems exhibit positive deviations from ideal behavior. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich−Kister, Van Laar, and Wisniak−Tamir equations.

The present work was undertaken to measure vapor−liquid equilibrium (VLE) data for the title systems for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for organic bromides.

Experimental Section

Purity of Materials. Cyclohexane (99.9+ mol %), heptane (99.82+ mol %), and 1-butanol (99.79+ mol %) were purchased from Merck, and 1-bromopropane (99.85+ mol %) was purchased from Frutarom. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*1*) was used in the VLE measurements. The experimental features have been described in a previous publication (*2*). All analyses were carried out by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, and the apparatus was operated under the conditions given in Table 2. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. Concentration measurements were accurate to better than ±0.008 mole fraction unit. The accuracy in determination of pressure P and temperature T was at least ±0.1 kPa and 0.02 K, respectively.

Table 1. GLC Purities (mol %), Refractive Index n_D at the Na D Line, and Normal Boiling Points T of the Pure Components

component (purity/mol %)	n_D(298.15 K)	T/K
1-butanol (99.79)	1.3972[a]	390.80[a]
	1.3973[b]	390.81[b]
cyclohexane (99.9)	1.4233[a]	353.84[a]
	1.42354[b]	353.888[b]
heptane (99.82)	1.3851[a]	371.46[a]
	1.38511[b]	371.574[b]
1-bromopropane (99.85)	1.4319[a]	343.90[a]
	1.4317[b]	344.15[b]

[a] Measured. [b] Reference 8.

Table 2. Gas-Chromatography Analysis

system	column filling	T/K		
		injector	column	detector
1-bromopropane + 1-butanol	OV-17	473.15	333.15	493.15
1-bromopropane + cyclohexane	SE-30	493.15	333.15	563.15
1-bromopropane + n-heptane	SE-30	523.15	343.15	553.15

Table 3. Experimental Vapor−Liquid Equilibrium Data for 1-Bromopropane (1) + Cyclohexane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
352.50	0.046	0.082	1.3970	1.0015
351.43	0.090	0.148	1.3285	1.0054
350.92	0.115	0.180	1.2831	1.0100
348.69	0.232	0.321	1.2098	1.0299
347.94	0.281	0.368	1.1705	1.0473
347.37	0.328	0.420	1.1637	1.0463
347.17	0.343	0.436	1.1621	1.0471
346.91	0.360	0.443	1.1337	1.0767
346.34	0.426	0.506	1.1128	1.0864
346.20	0.431	0.508	1.1089	1.0793
346.12	0.441	0.521	1.1141	1.0793
345.81	0.465	0.535	1.0951	1.1153
345.61	0.501	0.568	1.0855	1.1136
345.65	0.505	0.568	1.0756	1.1153
345.44	0.530	0.588	1.0676	1.1276
345.17	0.580	0.633	1.0587	1.1336
344.83	0.614	0.660	1.0534	1.1548
344.84	0.630	0.674	1.0473	1.1566
344.61	0.682	0.714	1.0327	1.1874
344.55	0.684	0.713	1.0301	1.2013
344.63	0.689	0.716	1.0245	1.2049
344.34	0.732	0.757	1.0284	1.2074
344.77	0.742	0.761	1.0067	1.2174
344.30	0.787	0.800	1.0121	1.2522
344.13	0.803	0.812	1.0120	1.2795
344.23	0.832	0.837	1.0037	1.2970
344.11	0.851	0.856	1.0072	1.2969
344.09	0.867	0.871	1.0065	1.3025
344.17	0.885	0.886	1.0006	1.3280
344.07	0.901	0.900	1.0014	1.3575
344.05	0.926	0.926	1.0031	1.3450
344.05	0.926	0.925	1.0020	1.3632
344.18	0.936	0.935	0.9981	1.3606
344.07	0.948	0.947	1.0014	1.3702
344.19	0.956	0.955	0.9978	1.3699
344.26	0.977	0.975	0.9948	1.4405

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at P = 101.3 kPa are

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Table 4. Experimental Vapor–Liquid Equilibrium Data for 1-Bromopropane (1) + Heptane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
369.33	0.032	0.086	1.3409	1.0054
367.62	0.062	0.156	1.3106	1.0059
366.40	0.087	0.209	1.2907	1.0032
365.32	0.107	0.247	1.2752	1.0074
363.31	0.150	0.325	1.2611	1.0065
362.54	0.164	0.340	1.2315	1.0237
360.39	0.224	0.426	1.1961	1.0233
359.11	0.254	0.468	1.1995	1.0258
358.36	0.275	0.485	1.1719	1.0455
357.79	0.297	0.514	1.1679	1.0356
354.71	0.394	0.617	1.1508	1.0427
351.77	0.525	0.711	1.0817	1.1030
351.21	0.546	0.728	1.0822	1.1061
349.25	0.650	0.792	1.0468	1.1702
348.87	0.666	0.797	1.0396	1.2118
348.44	0.694	0.817	1.0356	1.2097
347.76	0.737	0.843	1.0266	1.2354
346.72	0.803	0.880	1.0144	1.3056
346.53	0.819	0.889	1.0104	1.3230
345.67	0.877	0.924	1.0063	1.3727
345.51	0.897	0.935	1.0004	1.4098
344.82	0.951	0.969	0.9985	1.4476

Table 5. Experimental Vapor–Liquid Equilibrium Data for 1-Bromopropane (1) + 1-Butanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
379.89	0.058	0.357	2.3459	1.0139
378.60	0.062	0.377	2.3903	1.0360
374.52	0.095	0.500	2.2848	1.0093
373.49	0.110	0.530	2.1456	1.0048
369.79	0.142	0.601	2.0690	1.0265
363.98	0.222	0.730	1.8697	0.9760
362.90	0.235	0.730	1.8180	1.0394
358.45	0.323	0.805	1.6460	1.0303
356.88	0.345	0.818	1.6357	1.0661
355.20	0.398	0.835	1.5172	1.1347
352.48	0.475	0.866	1.4247	1.1976
351.79	0.515	0.873	1.3512	1.2689
349.27	0.644	0.902	1.2016	1.5027
348.93	0.655	0.906	1.1986	1.5118
348.11	0.705	0.917	1.1547	1.6239
347.61	0.740	0.923	1.1030	1.7991
347.39	0.759	0.933	1.0844	1.9093
346.81	0.794	0.933	1.0844	1.9993
346.38	0.827	0.940	1.0625	2.1772
346.28	0.830	0.943	1.0653	2.1153
345.81	0.868	0.949	1.0397	2.4943
345.40	0.903	0.961	1.0246	2.6488
344.91	0.944	0.974	1.0082	3.1341

reported in Tables 3 and Figures 1–6, together with the activity coefficients γ_i that were calculated from the following equation (*3*):

$$\ln \gamma_i = \ln \frac{y_i P_i^0}{x_i P} + \frac{(B_{ii} - v_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \quad (1)$$

where x_i and y_i are the equilibrium molar concentrations of component i in the liquid and vapor phases, T and P are the boiling point and the total pressure, v_i^{L} is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} = B_{jj} - B_{ii} \quad (2)$$

The pure component vapor pressures P_i^0 were calculated according to the Antoine equation:

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \quad (3)$$

where the constants A_i, B_i, and C_i are reported in Table 6.

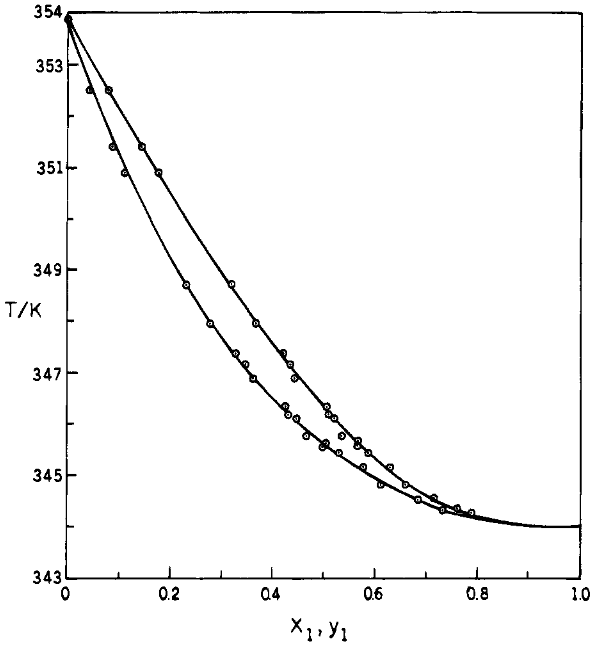

Figure 1. Boiling temperature diagram for the system 1-bromopropane (1) + cyclohexane (2) at 101.3 kPa.

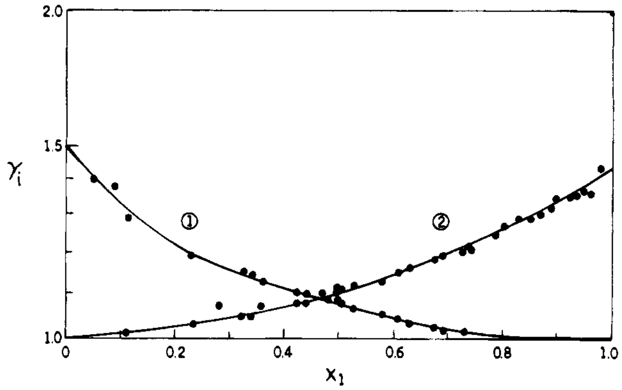

Figure 2. Activity coefficients for the system 1-bromopropane (1) + cyclohexane (2) at 101.3 kPa.

Table 6. Antoine Coefficients, Eq 3 (*7*)

compound	A_i	B_i	C_i
1-butanol	6.601 70	1362.39	94.38
cyclohexane	5.964 07	1200.310	50.65
heptane	6.021 67	1264.90	56.61
1-bromopropane	6.035 55	1194.889	47.64

The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz (*4*) using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in eq 1 contributed less than 3% to the activity coefficient, and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 3–5 and are estimated accurate to within ±3%. Inspection of Figure 1 points to the possibility of an azeotrope in the system 1-bromopropane + cyclohexane, which could not be investigated further because of limitations of the analytical method employed.

The vapor–liquid equilibrium data reported in Tables 3–5 were found to be thermodynamically consistent by the Redlich–Kister test (*5*) and by the L–W method of Wisniak (*6*). The activity coefficients for the different binaries were correlated as follows.

Table 7. Coefficients in Correlation of Boiling Points, Eq 8, Average Percent Deviation, and Root Mean Square Deviations in Temperature, rmsd(*T*/K)

system	C_0	C_1	C_2	C_3	rmsd[a]	av % dev[b]
1-bromopropane (1) + 1-butanol (2)	−58.573	37.464	−40.325	34.897	0.08	0.30
1-bromopropane (1) + cyclohexane (2)	−14.163	4.8161			0.02	0.11
1-bromopropane (1) + heptane (2)	−22.129	11.427	−5.2550		0.02	0.10

[a] Root mean square deviation. [b] Average percent deviation.

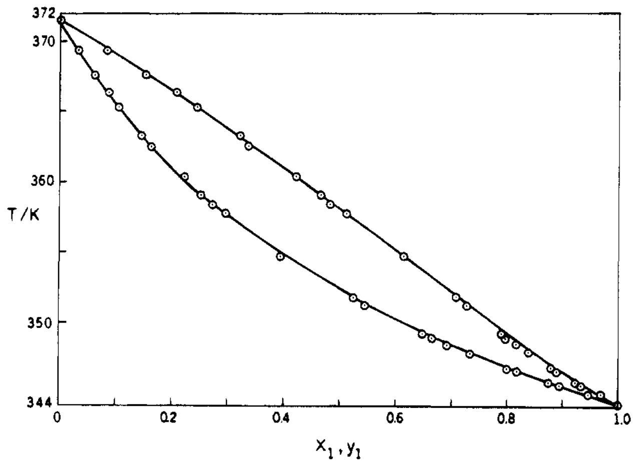

Figure 3. Boiling temperature diagram for the system 1-bromopropane (1) + heptane (2) at 101.3 kPa.

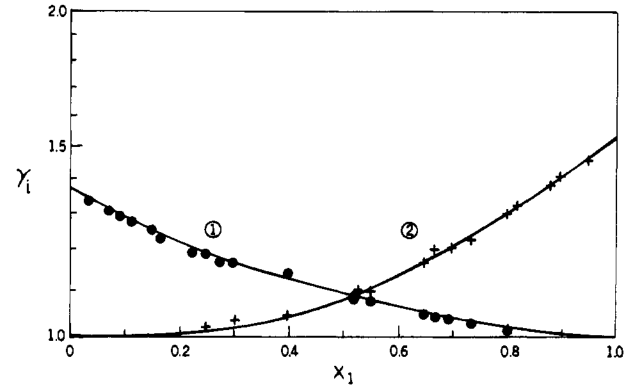

Figure 4. Activity coefficients for the system 1-bromopropane (1) + heptane (2) at 101.3 kPa.

(a) 1-Bromopropane (1) + 1-Butanol (2)

Van Laar expansion (*3*)

$$\log \gamma_1 = \frac{A}{\left[1 + \frac{x_1}{x_2}\frac{A}{B}\right]^2} \tag{4}$$

$$\log \gamma_2 = \frac{B}{\left[1 + \frac{x_2}{x_2}\frac{B}{A}\right]^2} \tag{5}$$

with A = 0.384 01, B = 0.611 58, an average percent deviation of less than 2, and a root mean square deviation (rmsd) of 0.010.

(b) 1-Bromopropane (1) + Cyclohexane (2)

Redlich–Kister expansion (*5*)

$$\ln \gamma_1/\gamma_2 = 0.1570(x_2 - x_1) - 0.0077(yx_1x_2 - 1) \tag{6}$$

with an average percent deviation of less than 1.5 and rmsd = 0.003.

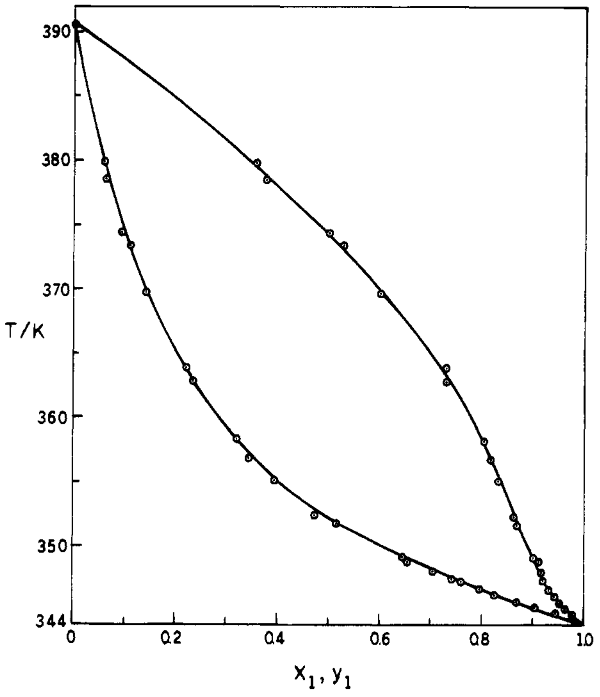

Figure 5. Boiling temperature diagram for the system 1-bromopropane (1) + 1-butanol (2) at 101.3 kPa.

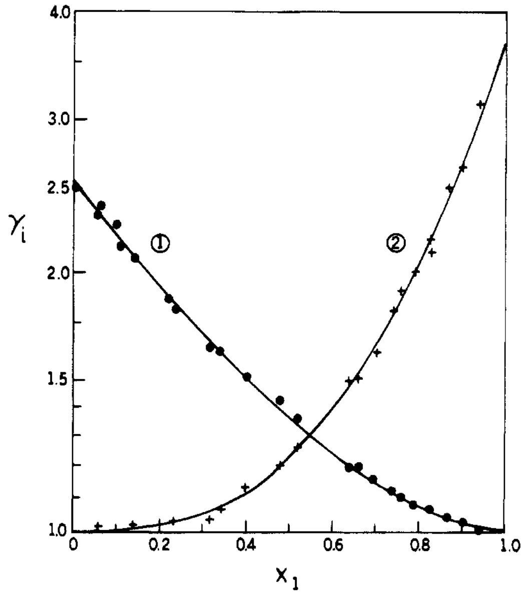

Figure 6. Activity coefficients for the system 1-bromopropane (1) + 1-butanol (2) at 101.3 kPa.

(c) 1-Bromopropane (1) + n-Hexane (2)

Redlich–Kister expansion (*5*)

$$\ln \gamma_1/\gamma_2 = 0.1542(x_2 - x_1) + 0.0217(6x_1x_2 - 1) \tag{7}$$

with an average percent deviation of less than 3 and rmsd = 0.007.

The boiling points of the three binaries were correlated by the equation proposed by Wisniak and Tamir (7):

$$T/\mathrm{K} = \sum_{i=1}^{2} x_i T_i^\circ/\mathrm{K} + x_1 x_2 \sum_{k}^{m} C_k (x_i - x_j)^k \qquad (8)$$

In this equation T_i^0 is the boiling point of the pure component i and m is the number of terms in the series expansion of $x_i - x_j$. The various constants of eq 8 are reported in Table 7, which also contains information indicating the degree of goodness of the correlation.

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