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Isobaric vapor–liquid equilibria in the binary systems propyl bromide–i-butanol, propyl bromide–1-chlorobutane and 1-chlorobutane–methyl ethyl ketone

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Abstract

Vapor–liquid equilibria at 101.3 kPa have been determined for binary systems propyl bromide–i-butanol, propyl bromide–1-chlorobutane and 1-chlorobutane–methyl ethyl ketone. The binary systems propyl bromide–i-butanol and 1-chlorobutane–methyl ethyl ketone exhibit positive deviations from ideal behavior while the binary system propyl bromide–1-chlorobutane behaves ideally. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich–Kister and Wisniak–Tamir equations.

Keywords: Activity; Activity coefficient; Binary system; Isobaric; VLE

List of symbols

A_i, B_i, C_i	Antoine constants, Eq. (3)
B_{ii}, B_{ij}	second molar virial coefficients, Eqs. (1), (2)
C_k	constants, Eq. (5)
N	number of measurements
P	total pressure
P_i^0	vapor pressure of pure component i
R	gas constant
rmsd(T)	root mean square deviation, $\{\sum(T_{\text{expt}} - T_{\text{calc}})^2\}^{0.5}/N$
t, T	boiling temperature of a mixture
t_i^0	boiling temperature of pure component i
v_i^{L}	molar volume of liquid component i

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x_i, y_i	mole fraction of component *i* in the liquid and vapor phases
γ_i	activity coefficient of component *i*

Subscripts

expt	experimental value
calc	calculated value
i	component *i*

1. Introduction

Aliphatic ketones and chlorobutanes are frequently used in the chemical industry as solvents and intermediates. The present work was undertaken to measure vapor–liquid equilibria (VLE) data for the title systems for which no isobaric data are available. This is part of a program to determine UNIFAC parameters for halogenated organic compounds.

2. Experimental

2.1. Purity of materials

Propyl bromide (99.85+ mol%), i-butanol (99.9+ mol%), 1-chlorobutane (99.84+ mol%) and methyl ethyl ketone (99.85+ mol%) were purchased from Merck. 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.

2.2 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 publica-

Table 1
Gas chromatography analysis

System	Column fling	Temperature/K		
		Injector	Column	Detector
Propyl bromide–i-butanol	Carbowax 20M	573.15	349.15	573.15
Propyl bromide–1-chlorobutane	SE-30	393.15	323.15	533.15
1-Chlorobutane–methyl ethyl ketone	SE-30	423.15	323.15	533.15

Table 2
Mol% GLC purities, refractive indices n_D at the Na D line, and normal boiling points T of pure components

Component (purity, mol%)	n_D(298.15 K)	T/K
Propyl bromide (99.85)	1.4316[a]	344.05[a]
	1.4317[b]	344.15[b]
i-Butanol (99.9)	1.3938[a]	380.79[a]
	1.3939[b]	380.81[b]
1-Chlorobutane (99.84)	1.3999[a]	351.58[a]
	1.4001[b]	351.58[b]
Methyl ethyl ketone (99.85)	1.3764[a]	352.71[a]
	1.3764[b]	352.79[b]

[a] Measured.
[b] Ref. [3].

tion [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 2 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 with gravimetrically prepared samples were carried out to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ± 0.008 mole fraction units. The accuracy in the determination of pressure P and temperature T was at least ± 0.1 kPa and 0.02 K, respectively.

Table 3
Experimental vapor–liquid equilibria data for propyl bromide (1) + i-butanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ cm^3 mol^{-1}	$-B_{22}$/ cm^3 mol^{-1}	$-B_{12}$/ cm^3 mol^{-1}
377.84	0.025	0.135	2.1602	0.9972	484	769	540
369.58	0.107	0.421	1.9335	0.9946	515	822	576
362.55	0.191	0.592	1.8321	1.0088	542	872	609
359.01	0.252	0.669	1.7276	1.0300	558	900	628
355.71	0.320	0.725	1.6154	1.0868	572	928	646
353.85	0.367	0.757	1.5507	1.1181	581	944	656
351.53	0.436	0.796	1.4656	1.1693	591	964	670
349.58	0.519	0.824	1.3497	1.2926	601	982	682
347.86	0.616	0.853	1.2383	1.4624	609	999	693
345.15	0.667	0.870	1.9132	1.5409	613	1006	697
345.48	0.779	0.899	1.1079	1.9575	621	1023	708
345.18	0.828	0.910	1.0653	2.2695	623	1036	710

3. Results

The temperature T and liquid phase x_i and vapor phase y_i mole fraction measurements at $P = 101.3\,\text{kPa}$ are reported in Tables 3–5 and Figs. 1–3, together with the activity coefficiens γ_i which were calculated from the following equation [4]

$$\text{Ln}\,\gamma_i = \text{Ln}\,\frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - v_i^{\text{L}})(P - P_i^0)}{RT} + y_j^2\,\frac{\delta_{12} P}{RT} \tag{1}$$

Table 4
Experimental vapor–liquid equilibrium data for propyl bromide (1) + 1-chlorobutane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ $\text{cm}^3\,\text{mol}^{-1}$	$-B_{22}$/ $\text{cm}^3\,\text{mol}^{-1}$	$-B_{12}$/ $\text{cm}^3\,\text{mol}^{-1}$
350.64	0.113	0.137	1.0012	1.0011	596	649	582
350.39	0.144	0.175	1.0107	0.9992	597	650	583
349.87	0.203	0.239	0.9939	1.0058	599	652	586
349.41	0.260	0.306	1.0068	1.0020	602	654	588
348.98	0.309	0.363	1.0182	0.9983	604	656	590
348.44	0.374	0.423	0.9952	1.0149	606	659	592
348.00	0.442	0.492	0.9992	1.0075	608	661	594
346.98	0.579	0.628	0.9962	1.0186	613	666	598
345.81	0.729	0.784	1.0228	0.9994	619	671	604
345.05	0.824	0.874	1.0321	0.9977	623	675	608

Table 5
Experimental vapor–liquid equilibrium data for 1-chlorobutane (1) + methyl ethyl ketone (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ $\text{cm}^3\,\text{mol}^{-1}$	$-B_{22}$/ $\text{cm}^3\,\text{mol}^{-1}$	$-B_{12}$/ $\text{cm}^3\,\text{mol}^{-1}$
352.04	0.060	0.074	1.2317	1.0074	643	1686	954
351.99	0.076	0.093	1.2232	1.0053	643	1687	954
351.84	0.082	0.100	1.2183	1.0092	644	1689	955
351.48	0.120	0.140	1.1830	1.0164	645	1694	958
351.35	0.153	0.174	1.1567	1.0184	646	1696	959
350.96	0.220	0.244	1.1393	1.0244	647	1702	962
350.60	0.299	0.325	1.1273	1.0295	649	1707	965
350.44	0.392	0.410	1.0883	1.0435	650	1709	966
350.40	0.436	0.450	1.0745	1.0505	650	1710	966
350.30	0.481	0.490	1.0631	1.0623	650	1712	967
350.27	0.588	0.572	1.0149	1.1255	650	1712	967
350.30	0.640	0.635	1.0335	1.0987	650	1712	967
350.46	0.759	0.742	1.0123	1.1571	650	1709	966
350.61	0.804	0.786	1.0074	1.1759	649	1707	965
350.88	0.867	0.853	1.0052	1.1827	648	1703	963
351.20	0.902	0.890	0.9983	1.1907	646	1698	960

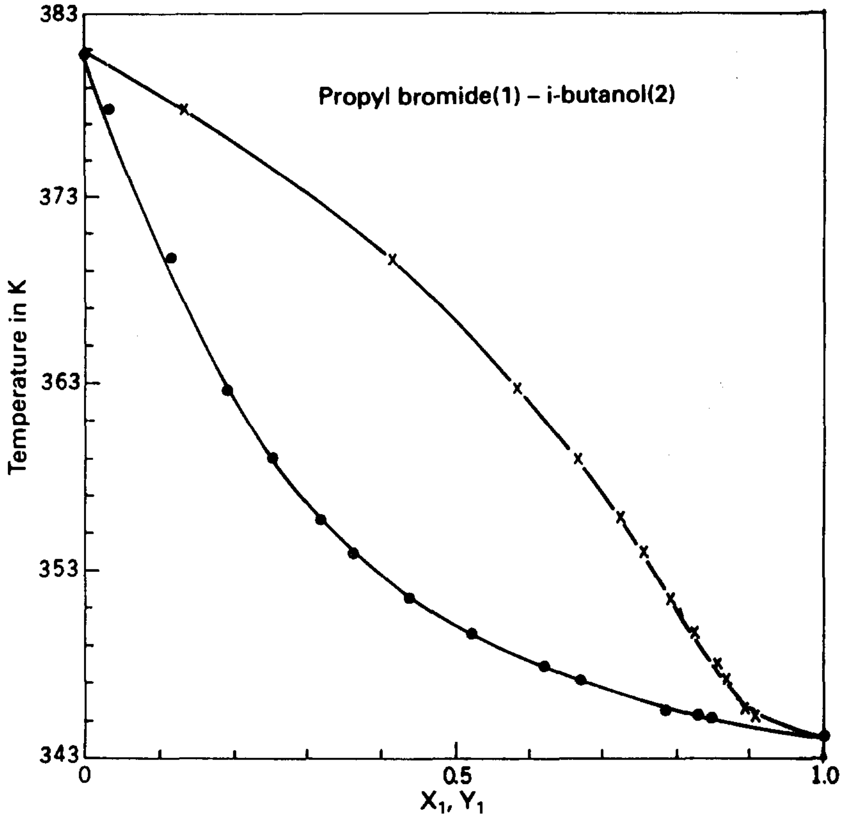

Fig. 1. Boiling temperature diagram for the system propyl bromide (1)–i-butanol (2) at 101.3 kPa.

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \tag{2}$$

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i^0 were calculated according to the Antoine equation

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

where the constants A_i, B_i, C_i are reported in Table 6. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of O'Connell and Prausnitz [5] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. The last two terms in Eq. (1) contribute less than 2% to the activity coefficient and their influence is important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 3–5 and are estimated to be accurate to within ±3%. The results indicate that the binary systems propyl bromide–

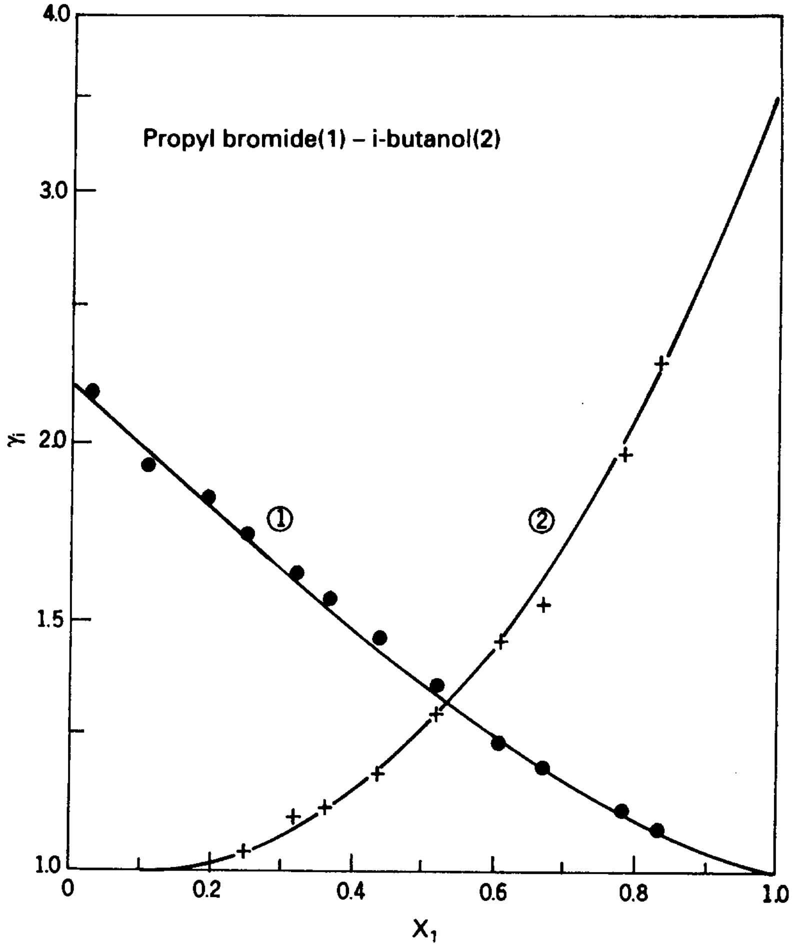

Fig. 2. Activity coefficients for the system propyl bromide (1)–i-butanol (2) at 101.3 kPa.

i-butanol and 1-chlorobutane–methyl ethyl ketone exhibit positive deviations from ideal behavior while the binary system propyl bromide–1-chlorobutane behaves ideally.

The vapor–liquid equilibria data reported in Table 3–5 were found to be thermodynamically consistent by the Redlich–Kister test [6] and by the L–W method of Wisniak [7]. The activity coefficients for the 1,3-dioxolane-chlorobutane binaries were correlated by the Redlich–Kister expansion [6]

$$\ln \gamma_1/\gamma_2 = B(x_2 - x_1) + C(6x_1x_2 - 1) + D(x_2 - x_1)(1 - 8x_1x_2) + E(x_2 - x_1)^2(10x_1x_2 - 1) \quad (4)$$

The values of the pertinent parameters and statistics appear in Table 7.

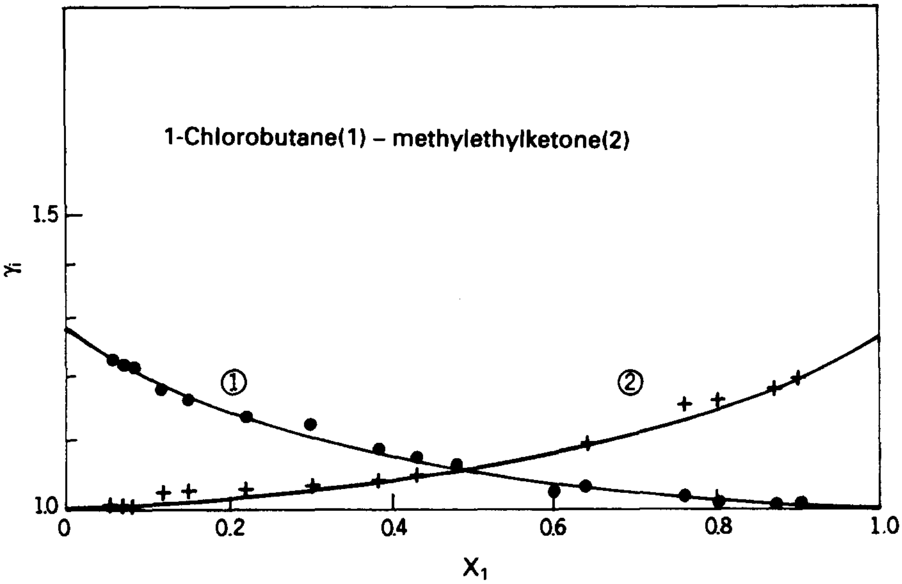

Fig. 3. Boiling temperature diagram for the system 1-Chlorobutane(1)–methyl ethyl ketone(2) at 101.3 kPa.

Table 6
Antoine coefficients, Eq. (3)[a]

Compound	A_i	B_i	C_i
Propyl bromide	6.03555	1194.889	47.64
i-Butanol	6.34504	1190.38	106.48
1-Chlorobutane	6.05154	1216.82	50.82
Methyl ethyl ketone	6.33358	1368.21	36.65

[a] Ref. [3].

Table 7
Redlich–Kister coefficients, Eq. (4)

System	B	C	D	rmsd	%[a]
Propyl bromide (1) + i-butanol (2)	0.4366	0.0855	−0.0018	0.01	1.9
1-Chlorobutane (1) + methyl ethyl ketone (2)	0.0958	−0.0091	−0.0102	0.01	1.3

[a] Average % deviation.

Table 8
.Coefficients in correlation of boiling points, Eq. (5), average % deviation and root mean square deviations in temperature, rmsd (T/K)

System	C_0	C_1	C_2	rmsd	%[a]
Propyl bromide (1) + i-butanol (2)	−50.032	27.954	−13.887	0.03	0.08
Propyl bromide (1) + 1-chlorobutane (2)	−1.0788	−0.31994	–	0.01	0.04
1-chlorobutane (1) + methyl ethyl ketone (2)	−7.7295	1.5989	–	0.02	0.07

[a] Average % deviation.

The boiling points of the three binaries were correlated by the equation proposed by Wisniak and Tamir [8]

$$T/\mathrm{K} = \sum_{i=1}^{2} x_i T_i^0/\mathrm{K} + x_1 x_2 \sum^{m} C_k (x_i - x_j)^k \tag{5}$$

In this equation, T_i^0 is the boiling point of the pure component i (K or °C) and m is the number of terms in the series expansion of $(x_i - x_j)$. The various constants of Eq. (5) are reported in Table 8 which also contains information indicating the degree of goodness of the correlation.

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