Vapor–Liquid Equilibria at 760 mmHg in the System Propyl Bromide–Toluene

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Vapor–liquid equilibria for the title system have been determined at 760 mmHg. The system shows slight negative deviations from ideal behavior. The boiling points were well correlated with the composition of the liquid phase.

The present work is part of our program for determining VLE data for organic systems in which one of the components is a bromide.

Experimental Section

Purity of Materials. Propyl bromide (99.6+ %) was supplied by Bromine Compounds Ltd., Beer-Sheva, and analytical grade toluene (99.6% +) was purchased from Frutarom. The reagents were used without further purification after gas chromatography analysis failed to show any significant impurities. Properties of the components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak–Boublik recirculation still (1) was used in the equilibrium determinations. The experimental details have been described previously (2). All analyses were carried out by gas chromatography on a Packard-Becker 417 apparatus provided with thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV-17 and operated isothermally at 95 °C. Injector and detector temperatures were 220 and 240 °C, respectively. Very good separation was achieved with helium as the gas carrier, and calibration analyses were carried to convert the peak area ratio to composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracies in the determination of pressure and temperature were $\Delta P = \pm 2$ mmHg and $\Delta T = \pm 0.02$ °C.

Results

The temperature–concentration measurements are reported in Table II and Figure 1. The activity coefficients were calculated from the following equations:

$$\ln \gamma_1 = \ln (Py_1/P_1^0 x_1) + (B_{11} - v^L_1)(P - P_1^0)/RT + P(1 - y_1)^2 \delta_{12}/RT \quad (1)$$

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

Vapor pressures of the pure components, P_i^0, were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(t + \delta_i) \quad (3)$$

the constants of which appear in Table III (3). The virial coefficients B_{11}, B_{22}, and B_{12} were estimated by the method of Tsonopoulos (4, 5), using the molar parameters suggested by the author.

Table I. Physical Properties of Pure Components

compound	refract index (25 °C)	normal boiling point, °C
propyl bromide	1.4300[a]	70.55[a]
	1.4302[b]	70.80[b]
toluene	1.4940[a]	110.7[a]
	1.4935[b]	110.8[b]

[a] This work. [b] Reference 3.

Table II. Experimental Vapor–Liquid Equilibrium Data for Propyl Bromide (1)–Toluene (2) at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
108.2	0.046	0.095	0.7734	1.015
107.43	0.061	0.125	0.7807	1.018
103.42	0.141	0.280	0.8317	1.025
102.32	0.155	0.315	0.8740	1.023
100.12	0.193	0.380	0.8933	1.033
98.15	0.230	0.450	0.9318	1.018
96.86	0.250	0.475	0.9345	1.037
95.16	0.288	0.530	0.9447	1.029
94.47	0.298	0.555	0.9730	1.009
91.32	0.360	0.635	0.9994	0.9995
89.48	0.400	0.685	1.0181	0.9745
87.46	0.440	0.715	1.007	1.012
87.40	0.445	0.725	1.024	0.9821
84.60	0.530	0.775	1.038	0.9545
82.80	0.585	0.825	1.0040	0.9698
82.77	0.590	0.826	0.9770	1.021
81.95	0.595	0.834	0.9694	1.043
80.82	0.640	0.860	0.9549	0.9386
79.03	0.700	0.892	1.008	0.8691
77.70	0.755	0.920	1.001	0.8905
76.82	0.755	0.930	1.011	0.8743
74.48	0.870	0.964	0.9994	0.8436
74.14	0.885	0.969	0.9975	0.8310

Table III. Antoine Constants[a]

	α_i	β_i	δ_i
propyl bromide	6.910 65	1194.889	225.51
toluene	6.953 34	1343.943	219.377

[a] Reference 3.

The activity coefficients reported in Table II are thermodynamically consistent and show that the system has a small negative deviation from Raoult's law.

The boiling points of the binary system were correlated by the equation suggested by Wisniak and Tamir (6):

$$T = x_1 T_1 + x_2 T_2 + x_1 x_2 [C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2 + ...] \quad (4)$$

An optimization technique yielded the following values for the constants: $C_0 = -20.291$, $C_1 = 4.4036$, and $C_2 = 12.665$, with an rmsd of 0.21. Boiling points were also correlated by another equation proposed by Wisniak (7):

$$T = x_1 T_1 + x_2 T_2 + A x_1 x_2 \exp(-B x_1) \quad (5)$$

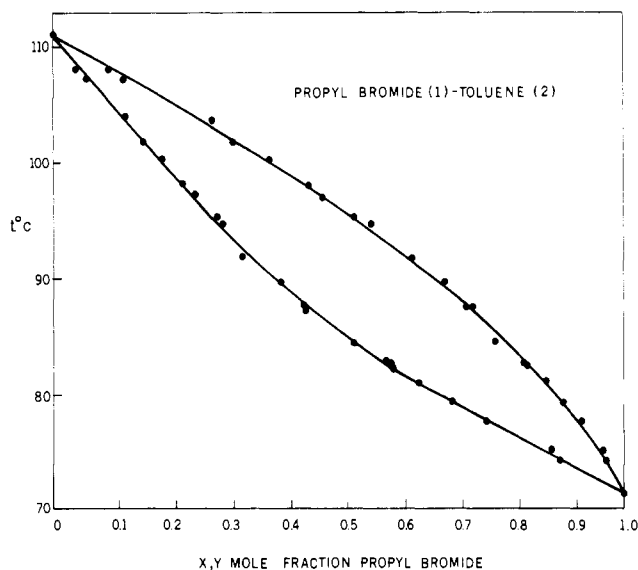The constants were determined to be $A = -28.603$ and $B = 0.837 76$, with $R^2 = 0.84$.

PROPYL BROMIDE (1)-TOLUENE (2)

X,Y MOLE FRACTION PROPYL BROMIDE

Figure 1. Boiling points diagram.

Glossary

α, β, δ	constants
B_{ii}, B_{ij}	virial coefficient
n	number of experimental points
P	overall pressure, mmHg
P_i^0	vapor pressure of pure component, mmHg
R	gas constant
rmsd	root mean square deviation $[\sum(T_{exptl} - T_{calcd})^2]^{1/2}/n$
t, T	temperature, °C, K
V^L_i	molar volume of pure liquid i, mL/mol
x_i, y_i	molar fraction of component i in the liquid and vapor phases
γ_i	activity coefficient of component i

Subscripts

calcd	calculated
exptl	experimental
i, j, k	component i, j, k

Registry No. Propyl bromide, 106-94-5; toluene, 108-88-3.

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Ultrasonic Velocity, Adiabatic Compressibility, Apparent Molar Volume, and Apparent Molar Compressibility Properties of Ternary Mixtures Containing 2-Butoxyethanol, Water, and Benzene or Decane

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Ultrasonic velocities and densities were measured in ternary systems of 2-butoxyethanol–water–benzene and 2-butoxyethanol–water–decane as a function of composition. Adiabatic compressibility coefficients, excess adiabatic compressibility coefficients, apparent molar volumes, and apparent molar compressibilities were calculated from these data. Transitions from the single-phase region to the two-phase region were found to be continuous with respect to the above properties. The results indicate that the addition of benzene or decane affects the 2-butoxyethanol–water ("clathrate-like") structures observed in binary systems. Increased compressibilities were observed in certain regions of low concentrations of hydrocarbon and water where oil-in-water and water-in-oil microphases, respectively, are present. ¹H NMR experiments appear to confirm the presence of water-in-oil microphases.

Introduction

Alcohol and water mixtures show minima and maxima in their thermodynamic properties at low alcohol concentrations (1–7). It is believed that processes similar to micellization can occur in aqueous solutions of long hydrocarbon chain alcohols. "Clathrate-like" structures of alcohol and water also have been proposed at low concentrations of alcohol. At higher alcohol concentrations merged clathrate structures and aggregates of alcohols have been shown to occur (4, 8, 9). The presence of a hydrocarbon component can cause changes in these aggregates of water and alcohol sometimes leading to the inclusion of the hydrocarbon in the aggregates. Evidence for the hydrocarbon converting the clathrate-like structures into stable microphases has been observed (10–13). The characteristic features of these microphases are similar to those of microemulsions which occur in the presence of surfactant. Here the surfactant is believed to stabilize the microphases and thus aid in the formation of microemulsions (14).

The ultrasonic velocity, adiabatic compressibility coefficient, and excess adiabatic compressibility coefficient are being studied in order to determine how sensitive they are to pre-

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