J. Chem. Eng. Data **1984**, *29*, 19-20

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

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Vapor–liquid equilibrium for the binary propyl bromide–methyl butyrate has been determined at 760 mmHg. The system behaves almost ideally. Boiling points were correlated by two empirical relations.

The present work was undertaken as part of a project devoted to the determination of UNIFAC interaction parameters for bromine derivatives.

Experimental Section

Purity of Materials. Analytical-grade methyl butyrate (99%+) was purchased from Fluka, Switzerland; propyl bromide (99.6%+) was supplied by Bromine Compounds Ltd., Beer-Sheva. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure 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 features have been described previously (*2*). All analyses were carried out by gas chromatography on a Packard-Becker 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm diameter and was packed with 20% OV17 on 80–100 Supelcoport and operated isothermally at 75 °C.

The injector temperature was 160 °C and the detector operated at 150 mA and 170 °C. Calibration analyses were carried out to convert the peak area ratio to the weight composition of the mixture. Concentration measurements were generally accurate to ±0.5%. The accuracies in determination of pressure and temperature were $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.2$ °C.

Results

The temperature–concentration measurements at 760 mmHg are presented in Table II. Activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln (P y_i / P_i{}^\circ x_i) + (B_i - v_i{}^L)(P - P_i{}^\circ)/RT + P(1 - y_i)^2 \delta / RT \qquad (1)$$

where

$$\delta = 2B_{ij} - B_{ii} - B_{jj} \qquad (2)$$

Vapor pressures at $P_i{}^\circ$ were calculated according to Antoine's equation

$$\log P_i{}^\circ = \alpha_i - \beta_i/(t + \delta_i) \qquad (3)$$

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

Table I. Physical Properties of Pure Components

compd	refractive index at 20 °C	normal bp, °C
propyl bromide (1)	1.4316[a]	70.55[a]
	1.4317[b]	70.8[b]
methyl butyrate (2)	1.3878[a]	102.55[a]
	1.3874[b]	102.75[b]

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

Table II. Vapor–Liquid Equilibria and Activity Coefficients at 760 mmHg

temp, °C	x_1	y_1	γ_1	γ_2
72.35	0.902	0.962	1.02	1.05
72.46	0.889	0.956	1.04	1.08
73.47	0.837	0.934	1.04	1.05
74.00	0.820	0.928	1.03	1.02
74.08	0.809	0.920	1.04	1.06
74.88	0.781	0.906	1.03	1.06
78.40	0.650	0.834	1.03	1.03
80.03	0.563	0.785	1.07	1.01
81.00	0.534	0.764	1.07	1.01
82.56	0.491	0.714	1.04	1.06
83.18	0.465	0.700	1.06	1.04
85.05	0.398	0.649	1.08	1.01
85.60	0.373	0.601	1.06	1.08
87.14	0.338	0.572	1.07	1.05
88.00	0.320	0.545	1.05	1.05
91.23	0.237	0.443	1.05	1.04
94.02	0.176	0.336	1.00	1.05
94.21	0.170	0.320	0.98	1.06
95.28	0.132	0.260	1.00	1.06
97.07	0.085	0.205	1.17	1.03
98.68	0.067	0.142	0.98	1.04

Table III. Vapor-Pressure Constants (*3*)

compd	α_i	β_i	δ_i
propyl bromide (1)	6.910 65	1194.889	225.51
methyl butyrate (2)	6.981 54	1271.060	207.21

The activity coefficients reported in Table II show that the system propyl bromide (1)–methyl butyrate (2) presents very small deviations from ideal solution behavior. In general, the contribution of the third term in eq 1 was insignificant and the deviations from pure gas ideality accounted for the positive deviation of the activity coefficients.

Boiling points of the binary were correlated by the equations suggested by Wisniak and Tamir (*6*) and Tamir (*7*):

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

An optimization routine yielded the following values for the constants:

$$C_0 = -18.9847 \qquad C_1 = 6.0176 \qquad C_2 = -9.7187$$

with an rmsd of 0.092 81.

Boiling points were also correlated by a new two-constant equation proposed by Wisniak (*8*):

$$T = x_1 T_1{}^\circ + x_2 T_2{}^\circ + A x_1 x_2 \exp(-B x_1) \qquad (5)$$

The values of the constants were found to be $A = 27.828$ and $B = 0.62505$ with an rmsd of 0.110.

0021-9568/84/1729-0019$01.50/0

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

α, β, A, B, C	constants
B_i	second virial coefficient, cm^3/mol
n	number of experimental points
P	overall pressure, mmHg
P_i°	vapor pressure of pure component i, mmHg
R	gas constant
rmsd	root-mean-square deviation $(\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n)^{1/2}$
t	temperature, °C
T	temperature, K
T_i°	boiling point of pure component, K
v_i^L	molar volume of pure liquid component, cm^3/mol
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficients

Subscripts

exptl	experimental
calcd	calculated
i	component i

Registry No. Propyl bromide, 106-94-5; methyl butyrate, 623-42-7.

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Received for review November 23, 1982. Revised manuscript received June 1, 1983. Accepted July 25, 1983.

Molecular Diffusivity of Hydrogen Sulfide in Water

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The molecular diffusivity of hydrogen sulfide in pure water was measured at different temperatures and under atmospheric pressure by using a laminar jet. Experimental results are compared with those available in the literature and with the Stokes–Einstein relation. The diffusivity was found to vary from 1.53 × 10^{-5} cm^2/s at 15 °C to 2.32 × 10^{-5} cm^2/s at 35 °C.

Introduction

Hydrogen sulfide is one of the constituents of natural gas and refinery gas. It is usually required to remove H_2S to improve the quality of fuel gas, to decrease the poisoning rate of catalysts used in ammonia production, or to obtain pure sulfur after further processing in the Claus process. Data on the physical properties of hydrogen sulfide are important for absorber design for the sweetening process of natural and refinery gases.

The diffusivity of hydrogen sulfide gas has been investigated by a few workers (*1–5*); however, there is disagreement in the literature on the values of the diffusivity, and the values available do not cover a wide range of temperature. In the work reported here a laminar jet apparatus is used to determine the molecular diffusivity of hydrogen sulfide in water at temperatures from 15 to 35 °C.

The laminar jet apparatus used in this work has several advantages compared to other laboratory absorbers. Its fluid dynamics are fairly well-known, and it is very versatile since the contact time and surface area can be easily varied by changing the jet length and liquid flow rate. The absorption rate into a laminar jet usually shows good agreement with the Higbie penetration theory.

Experimental Apparatus and Procedure

The experimental apparatus is shown schematically in Figure 1. The jet chamber consists of a 25.0 cm long, 4.4 cm i.d. glass tube. It is enclosed by a constant-temperature jacket which is constructed from a 25.0 cm long, 12.5 cm i.d. Plexiglas tube. The jet nozzle is a square-edged orifice, 0.051 cm in diameter, drilled in a 0.008 cm thick stainless steel sheet. The downstream face of the nozzle was coated with a thin layer of grease to prevent wetting. The solution is fed through the nozzle from a 1.9 cm i.d. glass tube. The nozzle is supported by a Teflon plate and fastened to a Teflon collar using two O rings and can be adjusted vertically. The receiver is a capillary tube of 0.1-cm i.d. and is fitted into a funnel-shaped Teflon base. A hole in the base allows draining of any liquid overflow. The jet is centered by three screws with rubber stoppers at their ends and surrounding the intake tube. A reservoir with a weir is used to keep the level constant in the capillary tube without an over- or underflow. The reservoir can be adjusted in the vertical direction. The length of the jet is measured by a precision vernier caliper with an accuracy of 0.0025 cm mounted on the top of the apparatus. The temperatures of the jet chamber and the water jacket were measured by a digital thermometer with ±0.1 °C accuracy. The apparatus was checked under 20 psi pressure and no leakage was detected.

Solutions used were deionized water. The H_2S used was CP grade from the Union Carbide Co. with a purity of 99.5%. Water was pumped by a constant-flow pump and its rate was measured by a calibrated rotameter. The gas stream was saturated with water after leaving the gas cylinder. Both water and gas streams were passed through separate coils maintained in the water jacket before entering the jet chamber.

Initially, air was removed from the jet chamber by displacement with water. H_2S gas was then introduced to the jet chamber while water was drained. Then the solution flow rate was fixed followed by adjustment of the liquid level in the capillary receiver. H_2S gas was allowed to flow into the jet chamber for a sufficient time until the required constant temperature was reached. Between experiments, the jet chamber was sealed off to prevent introducing air, and the chamber was purged again with H_2S at the beginning of each new experi-

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