Isothermal Vapor-Liquid Equilibrium Data for the System Formic Acid–Valeric Acid at 50°, 75°, and 100° C.

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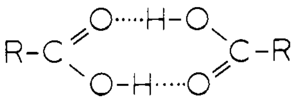
Isothermal equilibrium vapor and liquid composition measurements have been made for the formic acid–valeric acid system at 50°, 75°, and 100° C. Because the vapor phase behaves as a nonideal gas and since *PVT* data for the vapor are not available, it is not possible to check the thermodynamic consistency of the equilibrium data. Specific gravity measurements at 25° C. and refractive index measurements at 30° C. were also made for the system.

CARBOXYLIC acids are an unusual class of compounds because their vapors display nonideal behavior even at very low pressures. Acetic acid vapor, for example, has a compressibility factor of 0.755 at 92° C. and a pressure of 0.04 atmosphere (*7*). This nonideal behavior at low pressure is due to the acid vapor being partially associated through strong hydrogen bonding (*5*). The vapor phase hydrogen bonding produces a carboxylic acid dimer of the structure:



The extent of dimerization depends on the temperature and pressure of the system. At pressures below atmospheric, higher polymers do not appear to be present in the vapor to any significant extent (*5*).

A review of the literature indicates that vapor-liquid equilibrium data have been published for some carboxylic acid systems, but no data were found for the formic acid–valeric acid system. Isothermal equilibrium pressures and phase compositions have been obtained with the aid of a vapor recirculation still at 50°, 75°, and 100° C.

EXPERIMENTAL

Equipment and Materials. A vapor recirculation still of the type described by Hipkin and Myers (*3*) was used in this investigation. The desired still and jacket pressures were obtained and regulated with the aid of Cartesian manostats (*2*). The jacket and still pressures were read to the nearest 0.1 mm. of mercury on manometers equipped with vernier scales. The barometric pressure was read to the nearest 0.1 mm. with the aid of a vernier scale, thus giving an over-all precision of 0.2 mm. for the reported absolute pressures.

Copper-constantan thermocouples and a Leeds and Northrup Type K potentiometer were used to measure the equilibrium and jacket temperatures. The thermocouples were calibrated with pure heptane in the equilibrium still using the temperature-vapor pressure data tabulated in Dreisback (*1*). They were also compared with a mercury thermometer that could be read to the nearest 0.01° C.

Equilibrium samples were analyzed with a Bausch and Lomb Model 33-45-26-01 refractometer equipped with prism "B". The refractometer was used in conjunction with a sodium lamp, and a constant temperature bath was maintained at 30° ± 0.04° C.

The formic acid and valeric acid used were from K & K Laboratories, Inc. and Matheson, Coleman and Bell, respectively. Both had stated purities of 99.0% minimum. Measurements of the specific gravity and refractive index of these components and literature values are contained in Table I. Measured values of the vapor pressure of the formic acid are compared with literature values in Table II. The reagents were used without further purification.

Procedure. Composition–refractive index data were obtained by measuring the refractive index at 30° C. of solutions of formic and valeric acid that were compounded

Table I. Specific Volume, Refractive Index, and Composition Measurements for the Formic Acid, Valeric Acid System

Mole Fraction Formic Acid	Specific Gravity, Gram/Cc. at 25.0° C.	Refractive Index at 30.0° C.
0.0000	0.9331[a]	1.40417[a]
0.0937	0.9402	1.40194
0.1793	0.9492	1.39966
0.2838	0.9608	1.39715
0.3726	0.9722	1.39472
0.5196	0.9987	1.39019
0.5929	1.0147	1.38773
0.7065	1.0489	1.38351
0.7960	1.0826	1.37962
0.9061	1.1399	1.37362
0.9511	1.1709	1.37078
1.0000	1.2110[a]	1.36753[a]

[a] Values from the literature are: Valeric Acid: Specific Gravity (*1*) 0.9346 at 25° C. Refractive Index (*1*) 1.40200 at 30° C. Formic Acid: Specific Gravity (*6*) 1.2088 at 25° C. Refractive Index (*8*) 1.3671 at 30° C.

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Table II. Isothermal Vapor-Liquid Equilibrium Data for the System Formic Acid–Valeric Acid at 50°, 75°, and 100° C.

T, ° C.	P, mm. Hg	x_F	y_F	K_F	K_V
50.0	1.7[a]	0.000	0.000	...	1.000
	57.6	0.400	0.938	2.345	0.103
	68.7	0.498	0.955	1.918	0.090
	77.4	0.598	0.961	1.607	0.097
	87.3	0.678	0.969	1.429	0.096
	101.5	0.863	0.982	1.138	0.131
	109.8	0.913	0.988	1.082	0.138
	128.5[b]	1.000	1.000	1.00	...
75.0	7.6[a]	0.000	0.000	...	1.000
	81.5	0.198	0.838	4.232	0.202
	141.6	0.352	0.906	2.574	0.145
	172.9	0.426	0.924	2.169	0.132
	226.7	0.615	0.950	1.545	0.130
	237.2	0.666	0.954	1.432	0.138
	259.7	0.747	0.969	1.297	0.123
	294.9	0.905	0.979	1.082	0.221
	304.4	0.936	0.986	1.053	0.219
	331.2[c]	1.000	1.000	1.000	...
100.0	27.9[a]	0.000	0.000	...	1.000
	102.9	0.131	0.622	4.748	0.435
	146.8	0.142	0.738	5.197	0.305
	192.3	0.206	0.813	3.947	0.236
	221.6	0.217	0.813	3.747	0.239
	242.2	0.293	0.846	2.887	0.218
	270.1	0.313	0.858	2.741	0.207
	351.0	0.390	0.883	2.264	0.192
	403.9	0.464	0.905	1.950	0.177
	460.2	0.510	0.917	1.798	0.169
	462.8	0.508	0.918	1.807	0.167
	494.7	0.592	0.932	1.574	0.167
	561.0	0.697	0.943	1.353	0.188
	599.6	0.759	0.955	1.258	0.187
	665.2	0.886	0.973	1.098	0.237
	712.7	0.960	0.988	1.029	0.300
	741.2[d]	1.000	1.000	1.000	...

[a] Value from literature (*1*). [b] The literature value (*4*) is 128.5 mm. of Hg. [c] Value from literature (*4*). [d] The literature value (*4*) is 741.6 mm. of Hg.

to known compositions. A refractive index-composition plot that could be read to the nearest 0.1 mole % was prepared from the data. The refractive index-composition data are contained in Table I.

Specific gravities of the above samples were measured at 25° C. using a Seederer-Kohlbusch specific gravity balance. These specific gravities are contained in Table I.

The equilibrium still was charged and operated as suggested by Hipkin and Myers (*3*) with the exception that since the still was under vacuum, the system was quickly brought up to atmospheric pressure to stop the boiling before samples were drawn. The sample tubes were immersed in an ice bath to minimize evaporation losses.

The temperature of the still was controlled manually to better than ±0.1° C. The jacket fluid was toluene, and its temperature was maintained at or not more than 0.1° C. higher than the desired still temperature. When conditions in the still were such that there were no longer any significant variations in temperature and pressure, an additional 30 minutes were allowed to ensure equilibrium before samples were drawn.

Data were not obtained at pressures below about 50 mm. of Hg because of considerable bumping and uneven boiling which resulted in possible liquid entrainment from the vaporizer section to the vapor-liquid contactor.

The equilibrium temperature was recorded to the nearest 0.1° C., the pressure to 0.1 mm. of Hg, and the vapor liquid compositions to 0.1 mole %.

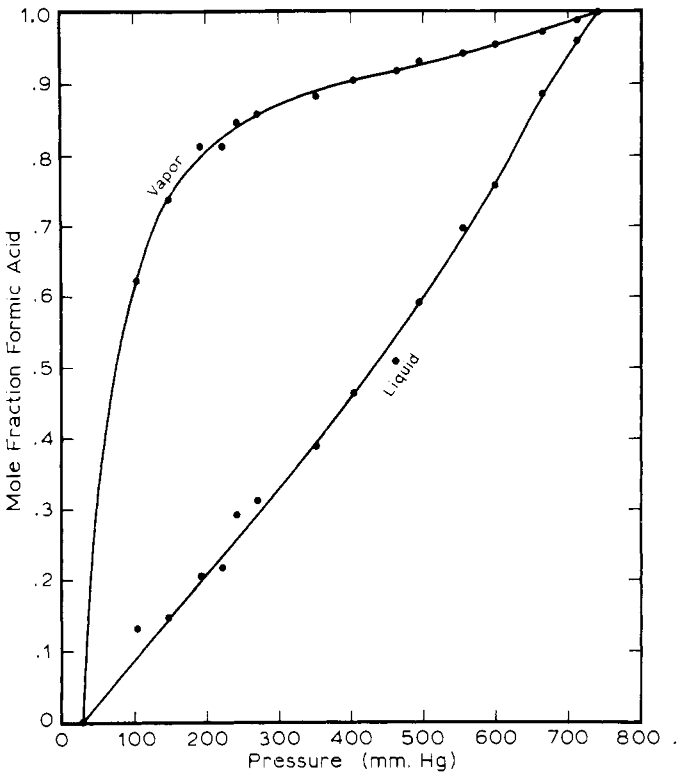

Figure 1. Isothermal vapor-liquid equilibrium compositions, and pressures for the formic acid–valeric acid system at 100° C.

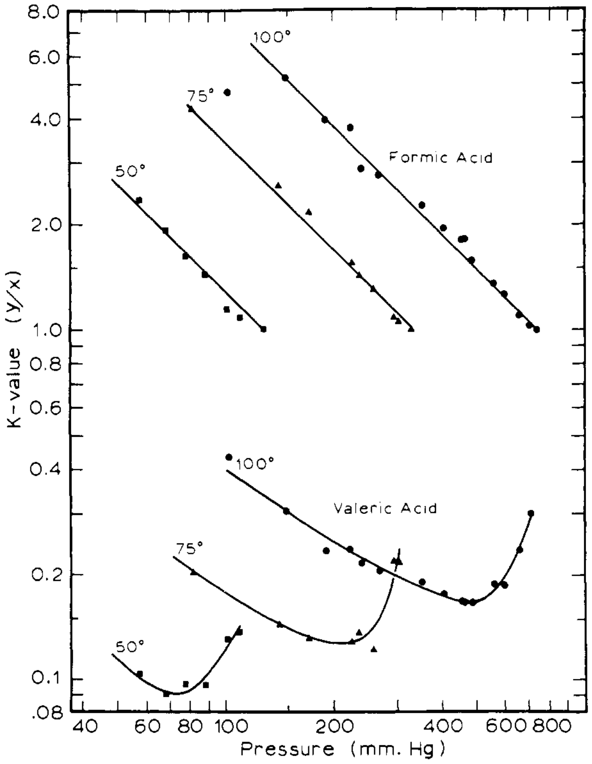

Figure 2. *K*-values for the formic acid–valeric acid system

DISCUSSION

Table II contains the experimental isothermal x, y, P equilibrium data obtained at 50°, 75°, and 100° C. Figure 1 is a plot of the equilibrium data at 100° C. and is typical of the data at 75° and 50° C. also. The vaporization equilibrium constants, K, for the formic acid and valeric acid at the three temperatures are tabulated in Table II and plotted against pressure in Figure 2. Neither of these plots indicates the presence of an azeotrope in the system.

Because the vapor phase of this system behaves as a nonideal gas and since PVT data for the vapor are not available, it is not possible to check the thermodynamic consistency of the data.

NOMENCLATURE

K = y/x = vaporization equilibrium constant
P = Pressure, mm. of Hg
T = Temperature, ° C.
x = Mole fraction in the liquid phase
y = Mole fraction in the vapor phase

Subscripts

F = formic acid
V = valeric acid

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Volumetric Properties of Supercritical Hydrogen Sulfide

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The volumetric properties of hydrogen sulfide were measured in a constant volume apparatus over the temperature range from 373° K. to 493° K. and a pressure range from 90 atm. to 1700 atm. The compressibility factors and virial coefficients at 20° intervals of this temperature range have been calculated. The virial expression given calculates the volumetric properties within 1% at temperature between 373° K. and 493° K. at pressures greater than 200 atm. and within 3% at pressures less than 200 atm. The density range covered by these measurements was between 8 and 24 moles per liter.

DURING the course of an investigation in the supercritical region of hydrogen sulfide, it became necessary to extend the region in which the volumetric properties of hydrogen sulfide were known. Thus, measurements in this laboratory, in the supercritical state only, extended the pressure range to 1700 atm. and the temperature range to 220° C. The results were expressed in the form of a virial equation in density.

Several investigations on the volumetric properties of hydrogen sulfide are reported in the literature. Giauque and Blue (*3*) measured the vapor pressure of hydrogen sulfide from 16° K. to the boiling point (212.8° K.). Cardoso (*1*) measured the vapor pressure of the coexisting phases between the boiling point (212.8° K.) and the critical point (373.6° K.). Beyond the critical point, Reamer, Sage, and Lacey (*5*) studied hydrogen sulfide to 171° C. and pressures to 680 atm.

EXPERIMENTAL

Measurements were made in a constant-volume apparatus having a total volume of 138.06 cc. This method was preferable to the variable volume method, because it circumvented the problem noted by Reamer, Sage, and Lacey (*4*) that the mercury used as a volume changing element reacted with the hydrogen sulfide at temperatures in the neighborhood of 170° C.

The stainless steel vessel and the associated fittings were manufactured by Pressure Products Industries (Hatboro, Pa.). Pressures were measured by an Astra Gauge Corporation Bourdon tube gauge that covered a pressure range from 0 to 30,000 p.s.i. and that had been calibrated to 0.25% accuracy of full scale against a dead weight gage at a minimum of five points. The dead weight gage was calibrated by the National Bureau of Standards for the Astra Corporation. The standard deviation in the piston and cylinder effective area was 57 p.p.m. The fractional change in the effective area per unit change in pressure was 8.85×10^{-9} p.s.i. with a standard deviation of 0.62×10^{-9} p.s.i. (NBS Monograph 65) (*2*). An oil bath, capable of maintaining the set temperature across the length of the vessel within ±0.5° C., was used to establish isothermal conditions during the course of the measurements. A mercury thermometer which had been calibrated against a copper-constantan thermocouple in a stirred oil bath was used for temperature measurement. The copper-constantan thermocouple was calibrated in accordance with NBS circular 590 (*6*) (ice point and boiling point of H_2O as primary points, freezing points of mercury and tin as secondary

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