To be submitted to: *Fluid Phase Equilibria*

The Vapor Pressure of Pure and Aqueous Glutaraldehyde

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Keywords: data, experiment, Henry's constant, 1,5-pentanedial, vapor-liquid equilibria (VLE), vapor pressure

ABSTRACT

A recirculating equilibrium still was used to measure pressure-temperature-liquid composition-vapor composition (PTxy) data on 18 dilute mixtures of water(1) + glutaraldehyde(2) between 38° and 85°C. The Henry's constants, $H_{2,1}$(kPa/mole fraction), derived from the PTxy data, were fitted by least-squares to give the equation, $\ln H_{2,1} = 29.1352 - 9187.99/T(K)$. To facilitate calculation of glutaraldehyde exposure during typical use, the Henry's constant correlation was used to compute concentrations of glutaraldehyde in air saturated by aqueous glutaraldehyde solutions. Vapor-pressure data for a dried sample of pure glutaraldehyde were measured in an ebulliometer between 55° and 163°C. An Antoine equation fitted to the intermediate temperature data between 74° and 109°C gives a normal boiling point for glutaraldehyde of 189.4°C and a 20°C vapor pressure of 0.044 kPa. The log vapor pressure vs 1/T(K) curve shows downward curvature at both the high-temperature and low-temperature ends. This suggests (i) a strong hydrogen-bonding effect at low temperatures and (ii) the possibility of polymerization of the sample at high temperatures. Finally, PTx data were measured in an ebulliometer for four aqueous mixtures between 10 and 50 mass per cent glutaraldehyde. Henry's constants derived from infinite-dilution activity coefficients from a Barker's method fit to the PTx data agree with the Henry's constants from the PTxy data.

INTRODUCTION

Glutaraldehyde (1,5-pentanedial; CAS Registry No., 111-30-8) is a reactive dialdehyde that is widely used as the active ingredient in biocides/disinfectants, tanning solutions, and film-processing aids. It is manufactured, stored, and used in aqueous solution. When pure glutaraldehyde is produced by drying the aqueous solution, the liquid glutaraldehyde sets to a glassy solid at room temperature within 24 h [1, 2]. The mobile liquid is recovered by heating and refluxing above 40°C.

Few vapor-pressure data have been measured on either pure or aqueous glutaraldehyde [3]. Secondary sources usually list two vapor-pressure points: NBP, 187-189°C, decomposes; 71-72°C at 1.33 kPa. This work reports measured vapor-pressure data of pure glutaraldehyde and glutaraldehyde partial-pressure data for aqueous solutions containing 50 ppm-mass to 50 weight per cent glutaraldehyde. From these data, the concentration of glutaraldehyde in air saturated by aqueous glutaraldehyde was calculated to aid in analysis of exposure to glutaraldehyde vapor in commercial applications.

EXPERIMENTAL SECTION

Aqueous solutions were synthesized by quantitative dilution of commercial Union Carbide Glutaraldehyde (50 Weight %) with distilled water. The pure glutaraldehyde sample was produced by evaporation of an aqueous solution at reduced pressure.

The PTxy apparatus is a modified Gillespie equilibrium still [4]. It is a one-stage distillation still that recirculates the liquid and vapor at total reflux. Dilute (50-500 ppm-mass) aqueous solutions of glutaraldehyde were charged to the still and refluxed for a

minimum of 3 h before samples of the liquid and condensed vapor were withdrawn. A 50-cc stirred-flask ebulliometer was used for the pure glutaraldehyde measurements and a twin vapor-lift-pump ebulliometer was used to measure PTx data for the 10-50 mass per cent aqueous mixtures. Pressures were controlled with a Mensor Model 10205 quartz manostat/manometer to ±0.007 kPa. Temperatures were measured: (i) to ±0.05°C in the stirred-flask ebulliometer with calibrated thermocouples, and (ii) to ±0.01°C in the twin vapor-lift-pump ebulliometer with a Hewlett-Packard Model 2804A quartz thermometer. Details of the ebulliometric procedures can be found elsewhere [5, 6].

The compositions of the liquid and condensed-vapor samples from the PTxy still experiments were analyzed by gas chromatography. The gas chromatograph is a Hewlett-Packard HP 5890 Series II with a FID detector. A 30 m x 0.53 mm J&W Megabore DB-5 column was used at 120°C with a nitrogen flow rate of 4.3 cc/min and a sample injection volume of 0.25 microliters. The gas chromatograph was calibrated with standards in the 50 ppm-mass to 600 ppm-mass range.

RESULTS

Table 1 contains results from four successive vapor-pressure experiments on a single sample of pure glutaraldehyde charged to the eublliometer. Antoine equations are given for least-squares fits to the first run and to all four runs.

Table 2 contains 18 PTxy measurements on dilute aqueous glutaraldehyde solutions at six temperatures between 38° and 85°C. The Pxy data at each temperature were

converted to partial pressure of glutaraldehyde, P_2, and to the Henry's constant, $H_{2,1}$(kPa/mole fraction), by the phase-equilibrium equation,

$$P_2 = y_2P = x_2H_{1,2} \quad (1)$$

with the assumptions that, at these low pressures, the vapor phase is an ideal gas and the liquid-phase properties are independent of pressure. The Henry's constant is the initial slope of the glutaraldehyde partial pressure vs composition curve.

Table 2 also contains the average $H_{2,1}(T)$ from a least-squares fit of Py_2/x_2 vs x_2 at each temperature. Figure 1 shows a least-squares fit of ln $H_{2,1}(T)$ vs 1/T(K) which produced a correlation equation with an R^2 of 0.999. The $H_{2,1}(T)$ equation,

$$\ln H_{2,1} = 29.1352 - 9187.99/T(K) \quad (2)$$

can be used to calculate $H_{2,1}(T)$ at temperatures down to 20°C as described below.

Table 3 contains 30 PTx measurements on aqueous mixtures of glutaraldehyde (and the water used to make the solutions). The difference between x, the liquid-phase mole fraction, and z, the overall mole fraction charged to the ebulliometer, shows the nearly negligible correction for vapor holdup and condensed-vapor holdup. Barker's method was used to fit the PTx data with a two-parameter Redlich-Kister activity coefficient model (Raoult's law reference state: pure liquid at system T and P). These data-reduction procedures have been discussed in detail [7, 8]. Infinite-dilution activity coefficients, γ_2^∞, thus derived at each pressure were converted to Henry's constants, $H_{2,1}(T)$, at each pure water boiling-point temperature by the equation,

$$H_{2,1} = \gamma_2^\infty P_2^{sat} \quad (3)$$

where P_2^{sat} is the pure glutaraldehyde vapor pressure. The values of the Barker's-method-derived g_2^{∞} increase with increasing temperature from g_2^{∞} = 3.5 at 38.3°C to g_2^{∞} =16.0 at 100.0°C. Figure 1 shows the $H_{2,1}(T)$ derived from the PTx data using Eq. 3 and P_2^{sat} from the Fit 1 vapor-pressure equation given in Table 1.

Table 4 contains concentrations in ppm-volume for glutaraldehyde in air saturated by aqueous glutaraldehyde solutions at a total pressure of 101.325 kPa and temperatures between 20° and 50°C. Saturated vapor concentrations were computed for aqueous solutions containing 100 and 1000 ppm-mass and 2, 15, and 50 mass per cent glutaraldehyde. The data were computed from Eq. 2 for the dilute solutions and from a 1-parameter Redlich-Kister model for the more concentrated solutions.

DISCUSSION

When analyzing vapor-pressure data and vapor-liquid equilibrium data for reactive chemicals like aldehydes, care must be taken not to mistake effects caused by irreversible chemical reactions (such as decomposition or polymerization) for effects due to the physical properties of the unreacted molecule.

The vapor-pressure experiments were carried out as successive P-T runs on one sample of glutaraldehyde charged to the ebulliometer. Note that the boiling points listed in Table 1 for Runs 2, 3, and 4 are slightly higher than those for Run 1. This suggests that some polymerization of the pure glutaraldehyde occurred in each cycle of the sample up and down in temperature. For that reason, the Antoine equation from Run 1 (Fit 1) is probably most reliable.

The downward curvature in the lower temperature vapor-pressure data of Runs 2 and 4 could also be due to the increased influence of hydrogen-bonding. This type of downward curvature in vapor-pressure data at lower temperatures is observed in experiments on strongly hydrogen-bonding molecules like acetic acid.

Glutaraldehyde has been shown to hydrogen-bond and polymerize with water. NMR and other studies [1-3, 9] have identified many hydrated, oligomeric, and polymerized structures of glutaraldehyde and water. The percentage of free dialdehyde molecules decreases as temperature of the aqueous solution decreases [9]. Because the concentration of these heavy water-glutaraldehyde species increases with decreasing temperature, the Henry's constant, $H_{2,1}(T)$, correlation shown in Figure 1 may predict an upper bound for $H_{2,1}(T)$ at lower temperatures. If there are actually fewer free dialdehyde molecules at 20°C than at the higher temperatures, $H_{2,1}(20)$ could be 0.7 or less of the value predicted from Eq. 2.

These vapor-pressure experiments on pure and aqueous glutaraldehyde and the literature NMR data suggest that extensive hydrogen-bonding increases the viscosity of pure glutaraldehyde exponentially as it is cooled. Therefore, pure glutaraldehyde becomes a glassy solid without freezing. However, in aqueous solutions, water (although a strongly hydrogen-bonding molecule) disrupts the intense specific forces present in the glassy solid glutaraldehyde.

In a recent work on aqueous formaldehyde mixtures, Maurer, et al., [10] showed that a distillation still may not attain chemical equilibrium among the oligomeric water + formaldehyde species at low temperatures. This is because the chemical reactions in

solution at low temperatures are slow compared to residence times in the different parts of the distillation equipment. Because of this effect, a recirculating PTxy still should not be used to measure low-temperature VLE on aldehyde solutions. The linearity of the PTxy ln $H_{2,1}(T)$ vs 1/T(K) data shown in Figure 1 suggest that these PTxy still data were measured at temperatures where equilibrium was attained.

In an earlier work, Hasse and Maurer [11] describe a gas-saturation apparatus to measure vapor-liquid equilibria of aqueous formaldehyde mixtures at low temperatures. Use of this apparatus avoids the possibility of not achieving chemical equilibrium in a recirculating PTxy still. This type of apparatus should be used if vapor-liquid equilibrium data on aqueous glutaraldehyde solutions are measured below 35°C.

The increasing g_2^∞ values with increasing temperature indicate that the effect of hydrogen bonding is diminished at higher temperatures. The effect of hydrophobic interaction between water and the five $-CH_2-$ groups in glutaraldehyde therefore increases with increasing temperature. In contrast, the corresponding five carbon mono-aldehyde, valeraldehyde, is hydrophobic enough at room temperature to produce liquid-liquid phase splitting.

Finally, the data in Table 4 indicate that the equilibrium saturation concentrations for some aqueous glutaraldehyde solutions are higher than the current TLV of 0.2 ppm [12]. However, for applications in a ventilated room, only a small fraction of the equilibrium saturation value is expected to be attained. Therefore, actual human exposure must always be monitored directly by air sampling. A recent review of air sampling studies is given by Dutton [13].

ACKNOWLEDGMENTS

J. K. Elkins measured the vapor pressure and VLE data and M. F. Stowers performed the gas-chromatographic chemical analysis.

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TABLE 1

Vapor-pressure data for glutaraldehyde

Run #	T (°C)	P (kPa)	P-Pcalc Fit 1	P-Pcalc Fit 2
1	74.2	1.33	0.01	0.05
	82.4	2.00	-0.01	0.03
	88.4	2.67	-0.01	0.01
	97.1	4.00	0.00	0.02
	103.6	5.33	0.01	0.05
	108.95	6.67	-0.01	0.07
2	54.6	0.35		-0.04
	63.4	0.67		-0.02
	79.1	1.67		0.00
	82.4	2.00		0.03
				0.00
3	97.2	4.00		
	119.7	10.00		-0.02
	127.7	13.33		-0.06
	163	40.00		0.01
4	56.8	0.40		-0.05
	66.7	0.80		-0.03
	73.6	1.20		-0.04
	79.5	1.67		-0.03
	93.2	3.33		0.00
	97.5	4.00		-0.05

Antoine Equation Least-Squares Fits (log10, °C, kPa)

	A	B	C	P(20°C)	T(101.325 kPa)
Fit 1 (Run 1 only)	7.0271852	2120.374	232.894	0.044	189.4
Fit 2 (All data)	5.1918763	1084.144	138.994	0.024	201.3

TABLE 2

Vapor-liquid equilibrium (PTxy) data for water(1) + glutaraldehyde(2)

T (°C)	P (kPa)	[Glut]-L ppm-mass	[Glut]-V ppm-mass	x_2	y_2	$H=Py_2/x_2$ (kPa)	H(fit) (kPa)
38.22	6.67	55.6	5.6	1.000E-05	1.004E-06	0.669	
38.22	6.67	120.3	12.2	2.165E-05	2.203E-06	0.678	0.678
45.88	10.00	55.6	7.6	1.001E-05	1.373E-06	1.372	
45.87	10.00	124.9	17.5	2.248E-05	3.147E-06	1.400	
45.92	10.00	590.4	78.8	1.063E-04	1.417E-05	1.334	1.340
49.47	12.00	57.9	10.8	1.042E-05	1.951E-06	2.247	
49.49	12.00	127.8	20.6	2.300E-05	3.709E-06	1.935	
49.49	12.00	561.8	108.0	1.011E-04	1.943E-05	2.305	1.953
60.08	20.00	57.4	14.4	1.034E-05	2.595E-06	5.020	
60.11	20.00	123.8	29.2	2.228E-05	5.246E-06	4.709	
60.11	20.00	557.5	144.4	1.004E-04	2.598E-05	5.178	
60.12	20.00	587.4	155.7	1.057E-04	2.802E-05	5.299	5.231
74.61	38.00	51.9	21.3	9.337E-06	3.828E-06	15.58	
74.60	38.00	108.5	40.8	1.953E-05	7.348E-06	14.29	
74.67	38.00	538.2	213.2	9.689E-05	3.838E-05	15.05	15.03
84.76	57.33	52.0	25.4	9.353E-06	4.568E-06	28.00	
84.76	57.33	121.1	69.5	2.179E-05	1.251E-05	32.92	
84.81	57.33	536.4	288.4	9.657E-05	5.191E-05	30.82	30.88

TABLE 3

PTx data for water(1) + glutaraldehyde(2)

z1	x1	T (°C)	P (kPa)	z1	x1	T (°C)	P (kPa)
0.8475	0.8411	40.46	6.666	0.8475	0.8416	53.65	13.332
0.9026	0.8991	39.67	6.666	0.9026	0.8994	53.00	13.332
0.9450	0.9432	39.24	6.666	0.9450	0.9433	52.49	13.332
0.9804	0.9799	38.71	6.666	0.9804	0.9799	52.00	13.332
1.0000	1.0000	38.28	6.666	1.0000	1.0000	51.64	13.332
0.8475	0.8428	77.47	39.997	0.8475	0.8427	84.42	53.329
0.9026	0.9001	77.02	39.997	0.9026	0.9001	84.02	53.329
0.9450	0.9437	76.58	39.997	0.9450	0.9438	83.64	53.329
0.9804	0.9801	76.11	39.997	0.9804	0.9801	83.21	53.329
1.0000	1.0000	75.82	39.997	1.0000	1.0000	0.00	53.329
0.8475	0.8431	90.05	66.661	0.8475	0.8433	101.13	101.325
0.9026	0.9004	89.69	66.661	0.9026	0.9005	100.92	101.325
0.9450	0.9439	89.27	66.661	0.9450	0.9441	100.51	101.325
0.9804	0.9801	88.94	66.661	0.9804	0.9802	100.25	101.325
1.0000	1.0000	88.66	66.661	1.0000	1.0000	100.0	101.325

TABLE 4

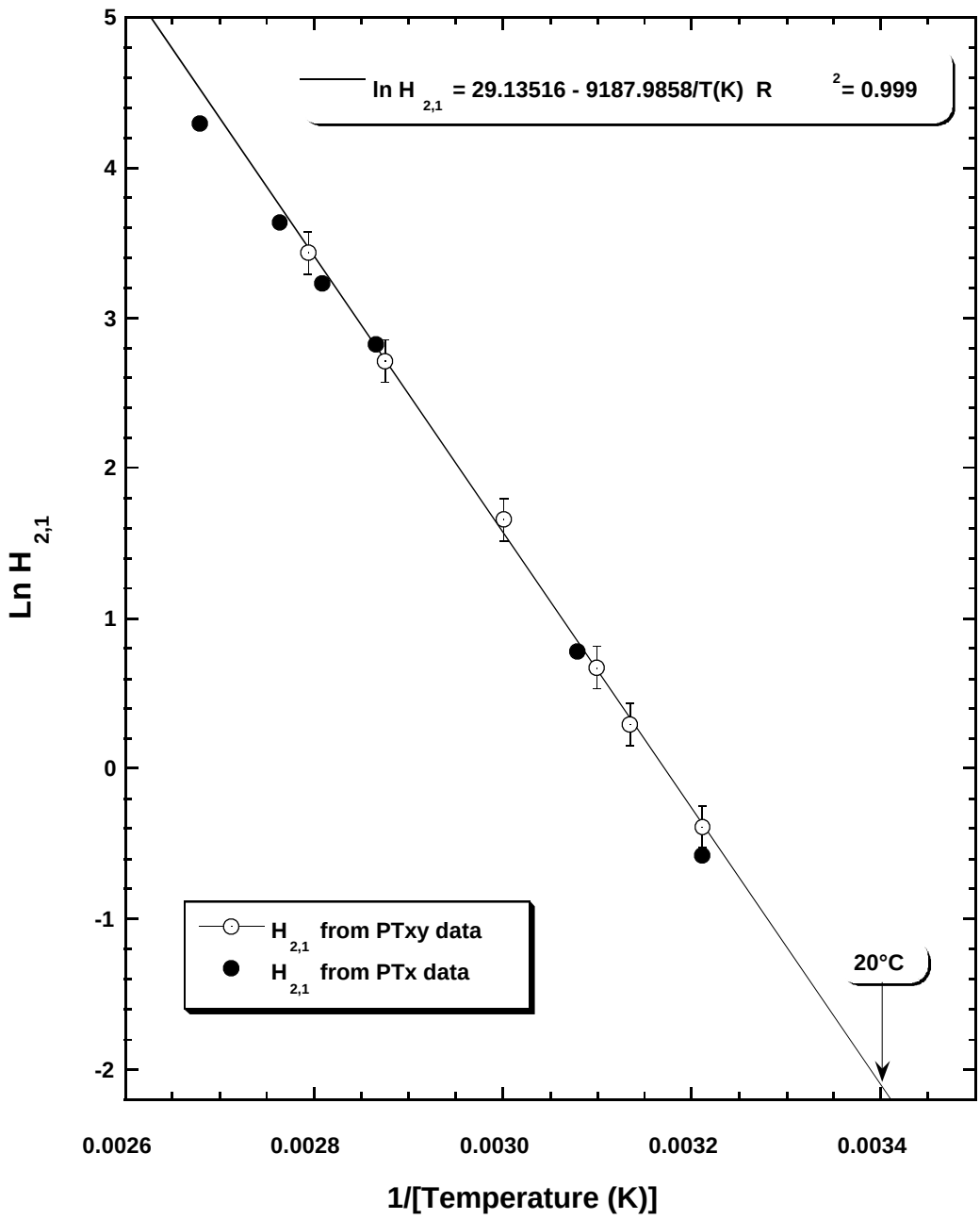
Glutaraldehyde concentrations in air saturated by aqueous glutaraldehyde solutions

[Glut]-liquid (mass %)	Glutaraldehyde ppm-volume in air						
	20°C	25°C	30°C	35°C	40°C	45°C	50°C
0.010	0.02	0.03	0.05	0.09	0.1	0.2	0.4
0.10	0.2	0.3	0.5	0.9	1	2	4
2.0	4	7	11	18	29	46	72
15.0	32	53	87	141	226	335	551
50.0	128	207	330	519	802	1223	1840

Total pressure = 101.325 kPa

FIGURE CAPTION

Figure 1. Henry's constant, $H_{2,1}$(kPa/mole fraction), for glutaraldehyde(2) dilute in water(1). The error bars represent ±15 per cent in the PTxy-derived $H_{2,1}$.


ln H 2,1 = 29.13516 - 9187.9858/T(K) R 2= 0.999
H 2,1 from PTxy data
H 2,1 from PTx data
20°C
Ln H 2,1
1/[Temperature (K)]
5
4
3
2
1
0
-1
-2
0.0026
0.0028
0.0030
0.0032
0.0034